

DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 43

HYDRATION OF PORTLAND CEMENT

BY

A. A. KLEIN, Assistant Physicist

and

A. J. PHILLIPS, Assistant Chemist

Bureau of Standards

[APRIL 18, 1914]



WASHINGTON
GOVERNMENT PRINTING OFFICE

1914

TECHNOLOGIC PAPERS OF THE BUREAU OF STANDARDS, DEPARTMENT OF COMMERCE

1. The Effect of Preliminary Heating Treatment upon the Drying of Clays (53 pp.)..... A. V. Bleining
2. The Strength of Reinforced Concrete Beams—Results of Tests of 333 Beams (first series) (200 pp.)..... R. L. Humphrey and L. H. Losse
3. Tests of the Absorptive and Permeable Properties of Portland Cement Mortars and Concretes, Together with Tests of Damp-Proofing and Water-Proofing Compounds and Materials (127 pp.)..... R. J. Wig and P. H. Bates
4. The Effect of Added Fatty and Other Oils upon the Carbonization of Mineral Lubricating Oils (14 pp.)..... C. E. Waters
5. The Effect of High-Pressure Steam on the Crushing Strength of Portland Cement Mortar and Concrete (25 pp.)..... R. J. Wig
6. The Determination of Chromium and Its Separation from Vanadium in Steels (6 pp.)..... J. R. Cain
7. The Testing of Clay Refractories, with Special Reference to Their Load-Carrying Capacities at Furnace Temperatures (78 pp.)..... A. V. Bleining and G. H. Brown
8. A Rapid Method for the Determination of Vanadium in Steels, Ores, etc., Based on Its Quantitative Inclusion by the Phosphomolybdate Precipitate (20 pp.)..... J. R. Cain and J. C. Hostetter
9. Density and Thermal Expansion of Linseed Oil and Turpentine (27 pp.)..... H. W. Bearce
10. Melting Points of Fire Bricks (17 pp.)..... C. W. Kanolt
11. Comparison of Five Methods Used to Measure Hardness (27 pp.)..... Ralph P. Devries
12. Action of the Salts in Alkali Water and Sea Water on Cements (157 pp.)..... P. H. Bates, A. J. Phillips, and R. J. Wig
13. The Evaporation Test for Mineral Lubricating and Transformer Oils (13 pp.)..... C. E. Waters
14. Legal Specifications for Illuminating Gas (31 pp.)..... E. B. Rosa and R. S. McBride
15. Surface Insulation of Pipes as a Means of Preventing Electrolysis (44 pp.)..... Burton McCollum and O. S. Peters
16. Manufacture of Lime (130 pp.)..... W. E. Emley
17. The Function of Time in the Vitrification of Clays (26 pp.)..... G. H. Brown and G. A. Murray
18. Electrolysis in Concrete (137 pp.)..... E. B. Rosa, Burton McCollum, and O. S. Peters
19. Physical Testing of Cotton Yarns (31 pp.)..... W. S. Lewis
20. Determination of Sulphur in Illuminating Gas (46 pp.)..... R. S. McBride and E. R. Weaver
21. Dehydration of Clays (23 pp.)..... G. H. Brown and E. T. Montgomery
22. Effect of Overfiring upon the Structure of Clays (23 pp.)..... A. V. Bleining and E. T. Montgomery
23. Technical Control of the Colloidal Matter of Clays (118 pp.)..... H. E. Ashley
24. Determination of Phosphorus in Steels Containing Vanadium (11 pp.)..... J. R. Cain and F. H. Tucker
25. Electrolytic Corrosion of Iron in Soils (69 pp.)..... Burton McCollum and K. H. Logan
26. Earth Resistance and Its Relation to Electrolysis of Underground Structures. Burton McCollum and K. H. Logan
27. Special Studies in Electrolysis Mitigation (55 pp.)..... E. B. Rosa and Burton McCollum
28. Methods of Making Electrolysis Surveys..... Burton McCollum and G. H. Ahiborn
29. Variation in Results of Sieving with Standard Cement Sieves (16 pp.)..... R. J. Wig and J. C. Pearson
30. The Viscosity of Porcelain Bodies (9 pp.)..... A. V. Bleining and Paul Teetor
31. Some Leadless Boro-Silicate Glazes Maturing at about 1,100° C. (21 pp.)..... E. T. Montgomery
32. Special Studies in Electrolysis Mitigation, No. 2. Electrolysis from Electric Railway Currents and Its Prevention—Experimental Test on a System of Insulated Negative Feeders in St. Louis (34 pp.)..... E. B. Rosa, Burton McCollum, and K. H. Logan

(Continued on p. 3 of cover.)

DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 43

HYDRATION OF PORTLAND CEMENT

BY

A. A. KLEIN, Assistant Physicist

and

A. J. PHILLIPS, Assistant Chemist

Bureau of Standards

[APRIL 18, 1914]



WASHINGTON
GOVERNMENT PRINTING OFFICE

1914

ADDITIONAL COPIES
OF THIS PUBLICATION MAY BE PROCURED FROM
THE SUPERINTENDENT OF DOCUMENTS
GOVERNMENT PRINTING OFFICE
WASHINGTON, D. C.
AT
20 CENTS PER COPY

▽

HYDRATION OF PORTLAND CEMENT

By A. A. Klein and A. J. Phillips

CONTENTS

	Page.
I. INTRODUCTION.....	3
II. ALUMINATES.....	5
1. Preparation of compounds.....	5
2. Description of apparatus.....	6
3. Hydration of monocalcium aluminate ($\text{CaO} \cdot \text{Al}_2\text{O}_3$) with water....	7
4. Hydration of 5:3 calcium aluminate ($5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$) with water...	11
5. Hydration of tricalcium aluminate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3$) with water.....	14
6. Dialysis experiment.....	18
7. Hydration of tricalcium aluminate containing 5:3 calcium aluminate and free lime, with water.....	19
8. Hydration of lime (CaO).....	21
9. Aluminates hydrated with calcium hydroxide $\text{Ca}(\text{OH})_2$	23
10. Aluminates hydrated with calcium sulphate (CaSO_4).....	26
III. SILICATES (INCLUDING MIXTURES OF SILICATES AND ALUMINATES).....	35
1. Hydration of calcium metasilicate ($\text{CaO} \cdot \text{SiO}_2$).....	35
2. Hydration of gamma-calcium orthosilicate ($\gamma_2\text{CaO} \cdot \text{SiO}_2$).....	36
3. Hydration of beta-calcium orthosilicate ($\beta_2\text{CaO} \cdot \text{SiO}_2$).....	37
4. Hydration of beta-calcium orthosilicate and aluminates.....	42
5. Hydration of tricalcium silicate ($3\text{CaO} \cdot \text{SiO}_2$).....	46
6. Hydration of tricalcium silicate and aluminates.....	49
IV. PORTLAND CEMENT.....	51
V. SUMMARY.....	59

I. INTRODUCTION

The Geophysical Laboratory,¹ studying the ternary system, lime-silica-alumina, has established the constitution of all the definite combinations of lime and alumina, lime and silica, silica and alumina, and lime, silica, and alumina. Furthermore, this laboratory² has verified the work of the Geophysical Laboratory,

¹ J. Ind. Eng. Chem., **3**, pp. 211-227; April, 1911.

² Concrete-Cement Age, **2** (cement mill section), pp. 3-7; January, 1913.

and determined the compounds which are actually present in Portland-cement clinker. With the constitution of cement thus established, it was thought advisable to take up the study of the effect of various amounts of water and steam at atmospheric and higher pressures on the individual compounds of cement and on Portland cement itself.

The work consisted of the preparation of the constituent binary compounds, their hydration on microscope slides with an excess of water, their hydration in a cylinder with steam according to the method proposed by Bied,³ their hydration in the autoclave with steam at various temperatures and pressures, and the hydration of specimens molded with quantities of water approximating those used in normal consistency mixtures; all products thus formed being examined with the petrographic microscope to determine the changes taking place.

The treated products were the three aluminates, monocalcium aluminate ($\text{CaO} \cdot \text{Al}_2\text{O}_3$), 5:3 calcium aluminate ($5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$), and tricalcium aluminate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3$); four silicates, calcium metasilicate ($\text{CaO} \cdot \text{SiO}_2$), gamma-calcium orthosilicate ($7/2\text{CaO} \cdot \text{SiO}_2$), beta-calcium orthosilicate ($\beta_2\text{CaO} \cdot \text{SiO}_2$), and tricalcium silicate ($3\text{CaO} \cdot \text{SiO}_2$); free lime burned at different temperatures, a high silica cement, a low silica cement, a high iron cement, and a high magnesia cement. In addition to the above two white cements containing different percentages of water due to aeration were studied. Previous papers^{4 5} of this laboratory have shown that the magnesia enters into beta-calcium orthosilicate up to 6 per cent and into tricalcium aluminate up to 10 per cent, forming homogeneous compounds; also that cements containing 7.5 per cent magnesia show no distinctive magnesium compounds. Therefore in this work no silicates and aluminates containing magnesia were prepared, but commercial cements of high magnesia content were examined.

³ Proc. Int. Assoc. Testing Mat., 2 (9), p. 8; 1911.

⁴ Orig. Com., 8th Int. Cong. Applied Chem., 5, pp. 73-81; 1912.

⁵ Concrete-Cement Age, 4 (cement mill section); pp. 29, 33, 38; March, 1914.

II. ALUMINATES

1. PREPARATION OF COMPOUNDS

For the preparation of specimens of aluminates, chemically pure calcium carbonate and alumina were mixed in desired proportions with a little water, molded into hollow bars, and burned in an updraft kiln. A diagram of this is shown in Fig. 1. The furnace was built of common brick and the chamber lined with magnesite brick. The specimens rested on a horizontally placed brick and were heated by two Fletcher burners supplied with natural gas and compressed air, a thermocouple and galvanometer being used to control the temperature. The furnace was usually fired overnight with natural draft, the temperature^{5a} reaching 800–900° by morning. The

blast was then turned on, and in three to four hours the temperature was raised to that desired. Owing to the fact that the compressed air, and, in later work, the electric current, could be ob-

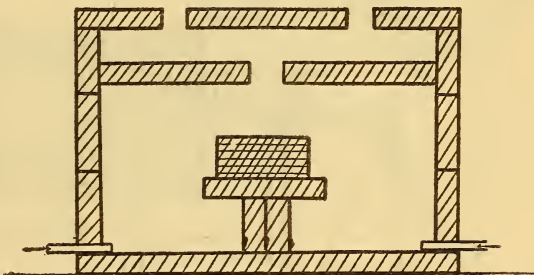


FIG. 1.—Showing up-draft kiln

tained for only eight hours a day at a maximum, it was impossible to bake the specimens continuously until a microscopic examination showed the desired homogeneity. Instead, the material was usually burned for one day, ground, examined, remolded and reburned, this process being repeated until the sample was satisfactory as regards homogeneity. Not over 400 grams of raw material were burned at one time. The resultant product was pulverized and sifted through a 200-mesh sieve before hydrating.

In no case was it possible to secure a homogeneous product by one burning in the furnace. At least two burnings with intermediate grindings were necessary. This must be borne in mind in view of the comparisons which are made with the results of other investigators of this problem, since, with few exceptions, they

^{5a} All temperatures in this work are given in the centigrade scale.

made no reburnings and no petrographical examinations. Consequently it is doubtful whether their products were homogeneous and has the desired constitution.

2. DESCRIPTION OF APPARATUS

The slides for observing hydration with excess of water were prepared in the following manner: A very small amount of the material to be hydrated was placed on a plane (not concave) slide, mixed with an excess of water, and covered with a thin cover glass.

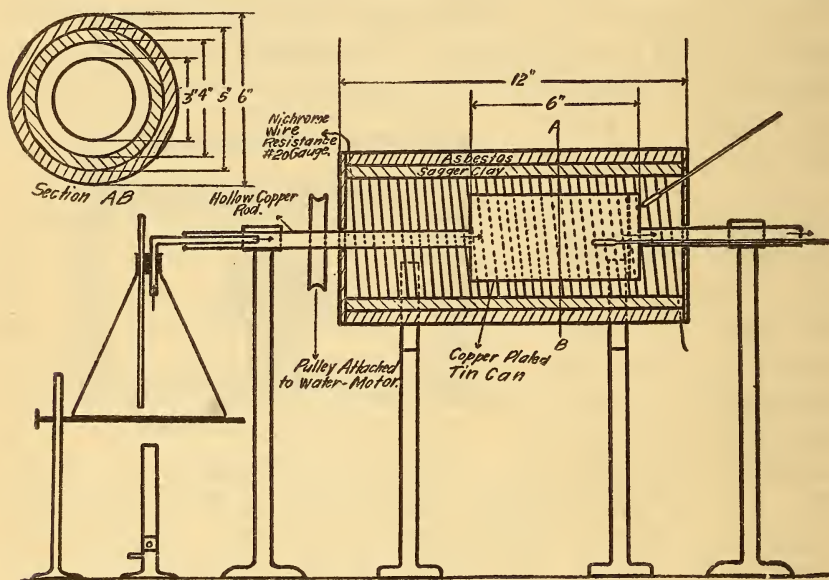


FIG. 2.—Showing apparatus for hydration in steam

Pressure was then applied on the latter so as to completely eliminate air bubbles, and the sides were carefully coated with a solution of Canada balsam in benzol or xylol (preferably the former because it evaporates more quickly). By this means evaporation and carbonation were prevented.

The apparatus (see Fig. 2) used for the hydration in steam at normal pressures consisted of a tin cylinder, through an opening in each end of which projected copper tubes. The cylinder was revolved in a nichrome resistance oven by a water motor at a speed of 20 revolutions per minute. The temperature inside this

cylinder and between the cylinder and the oven was read by means of mercury thermometers. The control of the temperature was rather difficult, owing to an endothermic reaction which started about 15 minutes after steam was first passed over the material; the inside thermometer in some cases showed a temperature of 100–105°, while the one outside the cylinder showed as much as 200°. Opening and closing the switch in the line supplying the current at intervals presented the most satisfactory method of regulating the temperature.

The autoclave consisted of a piece of steel pipe 18 inches long and 7 inches inside diameter closed at the top and bottom by caps. A gasket of asbestos cloth with wire insertion was used to make the joints withstand a pressure of 350 pounds per square inch. The pressure was indicated on a Fairbanks steam gauge.

3. HYDRATION OF MONOCALCIUM ALUMINATE WITH WATER

The monocalcium aluminate prepared consisted of irregular crystals which sometimes tended toward prismatic development. These were often irregularly intergrown, but twinning, described as a characteristic feature, was not observed. Indices of refraction were $\alpha = 1.642 \pm 0.003$, $\beta = 1.654 \pm 0.003$ and $\gamma = 1.660 \pm 0.003$. The measured double refraction gave $\gamma - \alpha = 0.018 \pm 0.003$. The maximum interference color observed was yellow of the second order. Biaxial interference figures were observed with a fairly small optic axial angle. No grains were found suitable for the quantitative determination of this angle. The optical character was negative. The chemical analysis showed:

	Per cent.
SiO ₂	0.46
Al ₂ O ₃	64.31
Fe ₂ O ₃16
CaO.....	34.94
Ignition loss.....	.15

(A) *Hydration on Slide (See Table 1).*—The monocalcium aluminate started to hydrate almost immediately. A transparent, amorphous mass first formed around the grains. Then radial spherulites and finally hexagonal plates and needles began to develop, both at the grains and away from them. These continued to grow and attained their maximum size in a few days,

and at the same time the amorphous material covered practically the whole slide. (See Fig. 3a, 3b.) The plates, needles, and spherulites were identical optically and chemically. They exhibited a medium double refraction and were uniaxial positive. The refractive indices were as follows: $\mu_e = 1.552 \pm 0.003$, $\mu_o = 1.535 \pm 0.003$. The character of the principal zone was positive. The needles were plates turned on edge, hence orientated parallel to the crystallographic "c" axis. The spherulites consisted of the needle crystals radiating from a common center.

A slide dried in an atmosphere free from carbon dioxide and tested for free lime and lime hydrate with White's reagent⁶ gave a negative result. Another slide, dried as above, was treated with an alcoholic solution of anthrapurpurine which according to Keisermann,⁷ dyes only free and combined lime. The needles, plates, and spherulites were dyed red, but the amorphous material was unchanged, showing that the latter contained no lime. Patent Blue, which, according to Keisermann, stains free and combined alumina, stained all the hydration products.

(B) *Hydration in Steam at Atmospheric Pressure.*—A 1-gram sample of monocalcium aluminate was placed in the can and rotated while the temperature was raised about 10° above that desired. Then steam was passed through the cylinder and temperature observations were made at frequent intervals. At the conclusion the steam was swept out by a current of natural gas, the cylinder was opened, and the contents were removed. The sample was dried for two hours on a steam plate at 100° in a current of air free from carbon dioxide. Operating in this manner it was possible to prevent the material from absorbing more than slight traces of carbon dioxide. Separate samples were used for each test. The amounts of water absorbed under the above conditions are given below and shown diagrammatically in Fig. 4.

	105°	110°	115°	120°
	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>
1 hour.....	12.00	2.00	0.5	Nil.
2 hours.....	16.00	4.99	1.3	0.10
4 hours.....	19.21	6.00	2.1	.15

⁶ J. Ind. Eng. Chem., 1, p. 5; 1909.

⁷ Cement Eng. News, 23, p. 10; January, 1911.

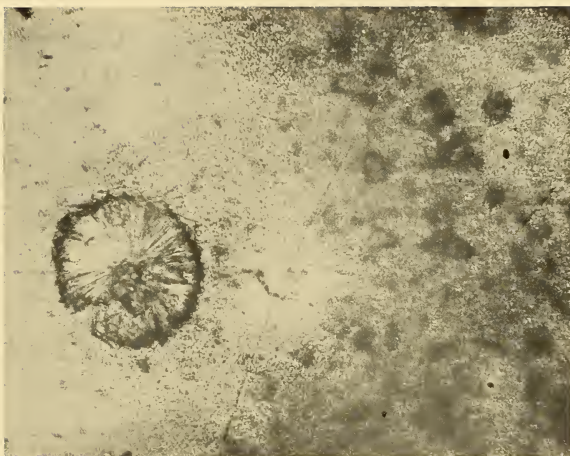


FIG. 3a.—Monocalcium aluminate in water taken without nicols and showing a large spherulite of hydrated tricalcium aluminate and amorphous hydrated alumina. The latter covers and obscures crystals of hydrated tricalcium aluminate. Magnification = 165 diameters

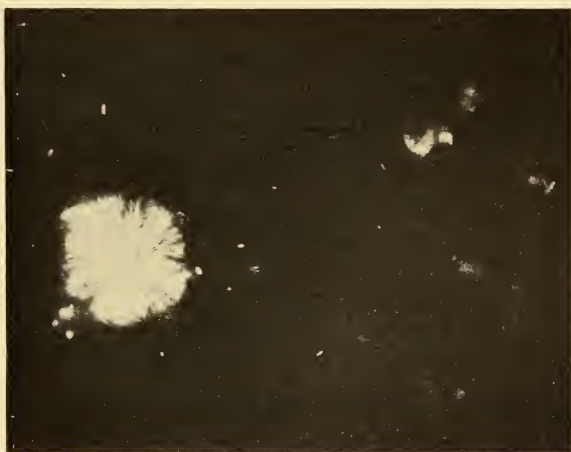


FIG. 3b.—This photograph is identical with figure 3a except that it was taken with crossed nicols. The amorphous material is invisible, but the crystals covered by it are clearly shown

The water absorption was greater at 105° than at any other temperature and confirms Bied's statement that the weakly basic aluminates do not absorb water appreciably above 110° . Hydration was not in any case complete, since the microscope showed unhydrated grains surrounded by and coated with a translucent mass of isotropic amorphous material and very fine needles. (The term amorphous and noncrystalline are used to designate any substance which shows no crystallization and is optically isotropic. This would include the colloidal material noted by previous investigators. It was thought best to avoid the use of the words colloid and colloidal material on account of the hazy and contradictory views concerning them set forth particularly by cement investigators.) With increase in duration of exposure up to four hours the needle crystals increased in number and size. The maximum interference color was yellow of the first order, and the crystals showed uniaxial interference figures. These crystals were identical with the needles observed on the slide and were identified as hydrated tricalcium aluminate (see hydration of tricalcium aluminate), indicating that amorphous alumina is split off and hydrated tricalcium aluminate is formed. With increase in temperature up to 140° more of the unhydrated monocalcium aluminate and less of the amorphous material was present. A sample of the material hydrated for four hours at 105° was heated for one hour in air to 160° , when the water content fell to 0.2 per cent and the fine needle crystals disappeared, though the isotropic material was still present.

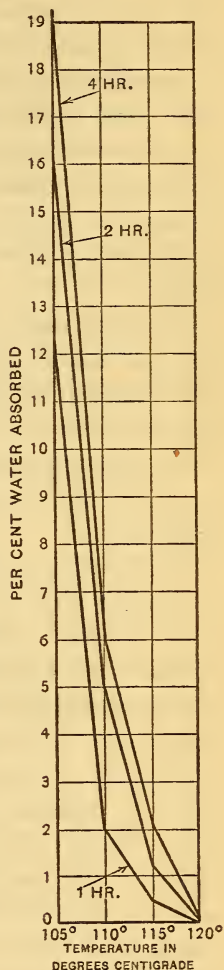


FIG. 4.—Showing the hydration of monocalcium aluminate in steam

(C) *Hydration in the Autoclave.*—A sample of the aluminate was stirred with a large excess of water in a porcelain crucible. This was covered, placed in the autoclave, and exposed to steam at 300 pounds pressure for two hours. After drying the specimen in the same manner as previously described it was examined microscopically and showed complete hydration with the formation of a large amount of the amorphous material and a very considerable quantity of needles and hexagonal plates of hydrated tricalcium aluminate. It is of significance that complete hydration occurred in so short a time and that considerable crystalline material was formed.

(D) *Hydration of Molded Specimens.*—Another sample of material was mixed with 30 per cent of water, pressed into a $\frac{1}{2}$ -inch cubical mold, and allowed to hydrate for 24 hours. At the end of this time it was very hard, being more difficult to powder than any of the other aluminates treated the same way. It consisted almost entirely of the amorphous material with a few of the needle crystals noted above.

The hydration of the monocalcium aluminate with splitting off of alumina is noted both by Schott⁸ and Keisermann.⁹ The fact that the final products of hydration are amorphous hydrated alumina and hydrated tricalcium aluminate is of importance and will be considered further under the discussion of calcium sulphoaluminate. Whether the hydrated tricalcium aluminate forms by the solution of monocalcium aluminate, splitting off of alumina and direct crystallization or from the conversion of amorphous tricalcium aluminate into crystalline material could not be determined, owing to the character of the material. The evidence, however, seems to point to the slow conversion of the amorphous aluminate which is of indeterminate composition into the crystalline variety some time after the hydrated alumina is split off. This latter view will be greatly strengthened when cements hydrated 7 and 28 days are considered. Stern¹⁰ calls attention to the fact that calcium aluminates are decomposed by water, forming calcium hydrate and gelatinous alumina, and if an aluminate is shaken with water

⁸ Cement Eng. News, **22**, p. 515; 1910.

⁹ Cement Eng. News, **23**, p. 10; January, 1911.

¹⁰ Chem. Ztg., **32**, pp. 1029-1031; 1908.

and filtered both lime and alumina are contained in the filtrate. If this filtrate be dialyzed, lime passes through the dialyzer generally without any alumina, although a trace of alumina may also pass through. The experiment of Stern was repeated (see page 18), but his results were not corroborated. Moreover, the aluminate was carefully tested by White's test ¹¹ in all stages of the hydration, and at no time was the presence of calcium hydrate detected.

In this connection mention might be made of the recent work of Blum ¹² on the constitution of aluminates. He studied the *H* ion concentration and electrical conductivity during the reaction of an aluminum salt with an alkali hydroxide. The results of this work add to the evidence in favor of the existence of definite aluminates in the solutions obtained by dissolving aluminum hydroxide in alkalies. This work is very interesting in view of the chemical similarity between the alkalies and the alkali earths.

4. HYDRATION OF 5:3 CALCIUM ALUMINATE WITH WATER

This aluminate was prepared in the usual way by mixing the materials in the proper proportion with a little water, molding into hollow cylinders, and burning them in the updraft kiln.

The sample, as prepared, consisted of irregular isotropic grains with a refractive index of about 1.61. Some of the crystals contained a few inclusions of double-refracting material with a higher index. The optical proportion of this material indicated that it was a mixture of monocalcium aluminate and the compound $2\text{CaO} \cdot \text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ ¹³. These crystals were prominent because of their marked difference from the large mass of isotropic crystals. The amount of these impurities was, however, very small, and their presence doubtless had no effect on the results obtained.

The chemical analysis showed:

	Per cent
SiO_2	0.28
Al_2O_3	51.92
Fe_2O_320
CaO	47.59
Ignition loss05

¹¹ J. Ind. Eng. Chem., 1, p. 5; 1909.

¹² J. Am. Chem. Soc., 85, p. 1499; October, 1913.

¹³ J. Ind. Eng. Chem., 3, No. 4, p. 40; April, 1911.

(A) *Hydration on Slide*.—The 5:3 calcium aluminate (see Figs. 5a and 5b) began to hydrate almost immediately, the first effect being the formation of an amorphous material around the grains and of spherulites away from the grains. The latter grew in size, and needles and plates, identical with those noted in the hydration of monocalcium aluminate, began to extend from them. These continued to increase in size and reached the maximum development after a few days. The amorphous material also increased in quantity, but the maximum amount was considerably less than that of the hydrated monocalcium aluminate. The amount of crystallized material, however, was much greater.

A slide of hydrated 5:3 calcium aluminate dehydrated in air free from carbon dioxide and treated with White's solution gave negative results. Another slide was similarly prepared. Part of it stained with anthrapurpurine showed absence of lime in the amorphous material, whereas the other portion stained with patent blue showed the presence of alumina in all the hydration products.

(B) *Hydration in Steam at Atmospheric Pressure*.—The quantities of water absorbed are given below and represented diagrammatically in Fig. 6:

	105°	110°	125°	140°
	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>
1 hour.....	11.08	8.21	3.10	0.27
2 hours.....	11.67	9.04	3.75	.34
4 hours.....	12.62	10.01	4.20	.39

At 105° a considerable amount of the material was changed and was coated with amorphous material and doubly refracting uniaxial needles. As the temperature increased the amount of amorphous material decreased, until at 140° there was extremely little of it present, and at 150° nothing but unchanged 5:3 aluminate was observed.

The silicate noted in this preparation of aluminate in all cases was unaffected by the steam treatment. The maximum water absorption occurred at 105°, but the amount was less than the corresponding absorption of the monocalcium aluminate. How-

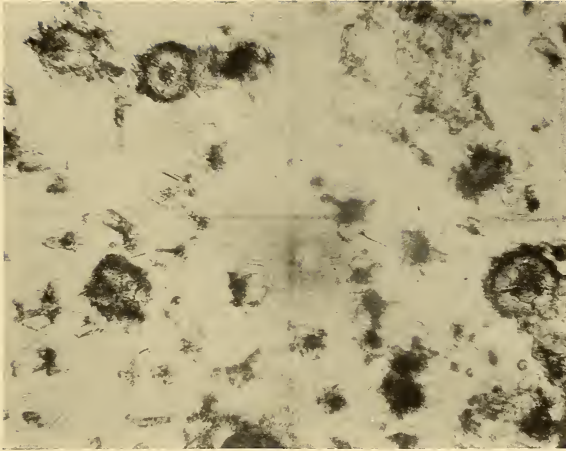


FIG. 5a.—5:3 calcium aluminate in water, showing needles, plates, and spherulites of hydrated tricalcium aluminate and amorphous hydrated alumina. This photograph was taken without nicols. Magnification = 180 diameters

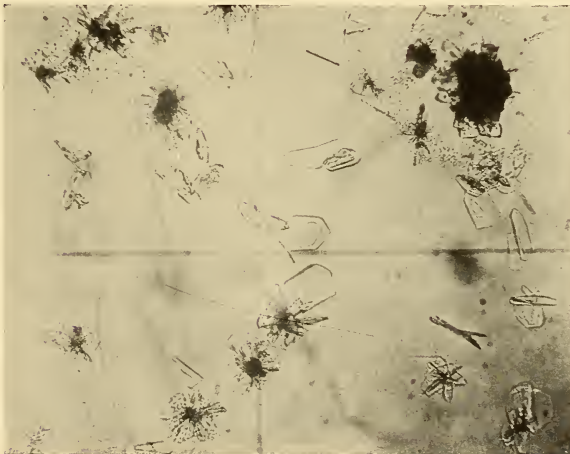


FIG. 5b.—5:3 calcium aluminate in water, showing needles and plates of hydrated tricalcium aluminate and amorphous hydrated alumina; taken without nicols. Magnification = 300 diameters



ever, the increase in lime content seems to allow the absorption of water at higher temperatures. The material hydrated at 110° was reheated to 160° in steam, and it was found that the needle crystals were destroyed.

(C) *Hydration in the Autoclave.*—For this test a sample of the material was stirred with water in a small porcelain crucible, covered and heated at 300 pounds for two hours in the autoclave. The results showed complete hydration with the formation of lath-shaped prismatic crystals, small hexagonal plate crystals, and a small amount of amorphous material. The optical properties of the crystals established them as hydrated tricalcium aluminate.

(D) *Hydration of Molded Specimens.*—Molding of specimens with 28 per cent of water showed after 24 hours very little development of crystals and much amorphous material. Variations in the water content thus simply cause varying amounts of crystalline material to be formed immediately on hydration, the resulting products in each case being identical.

One further fact concerning the hydration of 5:3 calcium aluminate is worthy of emphasis, namely, that the microscopical examination of the hydrated product revealed no free lime or lime hydrate, but that hydrated tricalcium aluminate was found in all cases. Cements usually contain some free lime and sometimes 5:3 calcium aluminate. Under these conditions it is probable that quantities of the hydrated aluminate would be formed by combination of calcium hydrate and the hydrated alumina split off from the 5:3 calcium aluminate, although such a process would seem to be a slow one. Kasai¹⁴ found that on addition of hydrated silica and alumina to cement only the former was of value. Yet the

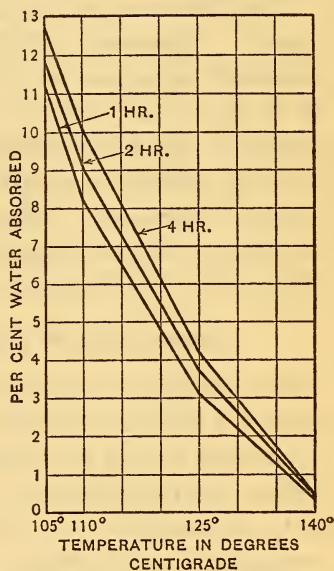


FIG. 6.—Showing the hydration of 5:3 calcium aluminate in steam

¹⁴ Cement, 17, pp. 41-44, 61-63; 1912.

action of the hydrated alumina, split off in the presence of calcium hydrate, can not be predicted from the combination of calcium hydrate and precipitated, washed alumina, as the two materials would differ materially in their behavior, owing to their different methods of formation. Gallo¹⁵ has already called attention to the formation, in puzzalona mortars, of a compound of the formula $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$ from soluble calcium aluminate in the presence of calcium hydrate.

The literature on the subject of the 5:3 calcium aluminate is scanty. Excepting Michaelis, who states that 5:3 calcium aluminate is present in cement, the only noteworthy mention made of it is in the work of the Geophysical Laboratory. Various hydration tests are found on the so-called dicalcium aluminate, but this usually is a mixture of 5:3 calcium aluminate and tricalcium aluminate. Where the product is fused, it consists of 5:3 calcium aluminate, tricalcium aluminate, and free lime, due to the dissociation of tricalcium aluminate.

5. HYDRATION OF TRICALCIUM ALUMINATE WITH WATER

More difficulty was experienced in securing a homogeneous specimen of tricalcium aluminate than of the other aluminates, owing to the fact that it was underburned at first, forming a soft porous clinker containing much free lime, a little tricalcium aluminate, and considerable 5:3 calcium aluminate. On pulverizing and regrinding and burning part of it fused. The microscopical examination of the fused product revealed the same constituents as in the underburned specimen, the only difference noted being a growth in size of the free lime grains. A third pulverization and burning resulted in a satisfactory specimen. It was found necessary, however, to hold the temperature at least 50° below the fusion point in order to secure the best results. The material yielded on analysis:

	Per cent.
SiO_2	0.48
Al_2O_3	37.78
Fe_2O_316
CaO	61.41
Ignition loss23

¹⁵ Gazz. Chim. Ital., 88, II, pp. 156-204; 1908.

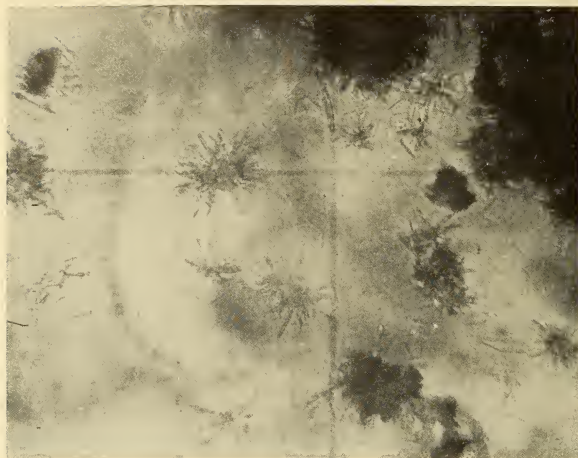


FIG. 7a.—Tricalcium aluminate in water, showing hexagonal plates, needles, and needle aggregates of hydrated tricalcium aluminate; taken without nicols. Note the absence of amorphous, hydrated alumina. Magnification = 250 diameters

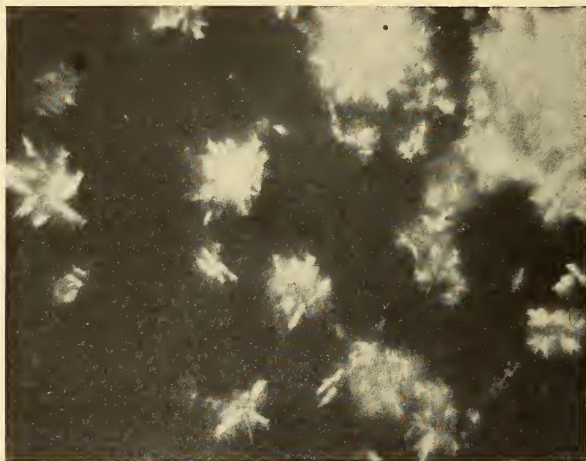


FIG. 7b.—This photograph is identical with figure 7a except that it was taken with crossed nicols. Note the crystallinity of the apparently amorphous aggregates

It consisted almost entirely of irregular to cubical isotropic grains, with the refractive index equal to 1.710. No definite cleavage was observed.

(A) *Hydration on Slide.*—Almost immediately fine needles and small hexagonal plates were formed at and away from the tricalcium aluminate grains (see figs. 7a and 7b). These were very minute at first, but grew in size and reached maximum growth at the end of a few days. The determination of their optical properties proved them to be identical with each other and also with the needles and plates observed in the hydration of the other aluminates. The plates were orientated perpendicular to the "C" crystallographic axis and the needles were orientated parallel to this axis. No amorphous hydration product was observed, this being in contradistinction to the observations with 5:3 calcium aluminate and monocalcium aluminate. A slide of hydrated tricalcium aluminate dried in an atmosphere free from carbon dioxide and treated with White's reagent, gave negative results. The absence of lime hydrate and amorphous hydrated alumina establishes the composition of this compound as hydrated tricalcium aluminate.

(B) *Hydration in Steam at Atmospheric Pressure.*—On exposure for four hours at 110° only a little tricalcium aluminate was hydrated. Some of the grains showed a border of doubly refracting material consisting of fairly well-developed needles and some plates of hydrated tricalcium aluminate, together with some amorphous material. Increasing the temperature to 140° served merely to lessen and prevent the formation of the crystals. The formation of the border of hydrated crystalline and noncrystalline material seems to indicate that the trialuminate goes first through an amorphous condition previous to crystallization. The amount of water absorbed by the three aluminates decreases as the lime content increases, and the large water absorption of monocalcium aluminate and 5:3 calcium aluminate is due to taking up of water by the amorphous hydrated alumina which is split off. White's test in every case failed to show the presence of calcium hydrate, so that again there was no evidence in favor of dissociation into calcium hydrate and hydrated alumina. The two reactions involved are simply the addition of water with formation of an

amorphous, hydrated aluminate, and the subsequent crystallization of this compound. Under the special conditions obtaining when tricalcium aluminate is hydrated on a slide with a large excess of water, the amorphous condition is either of very short duration, or else it is entirely lacking, and the material hydrates immediately as crystals of hydrated tricalcium aluminate. The

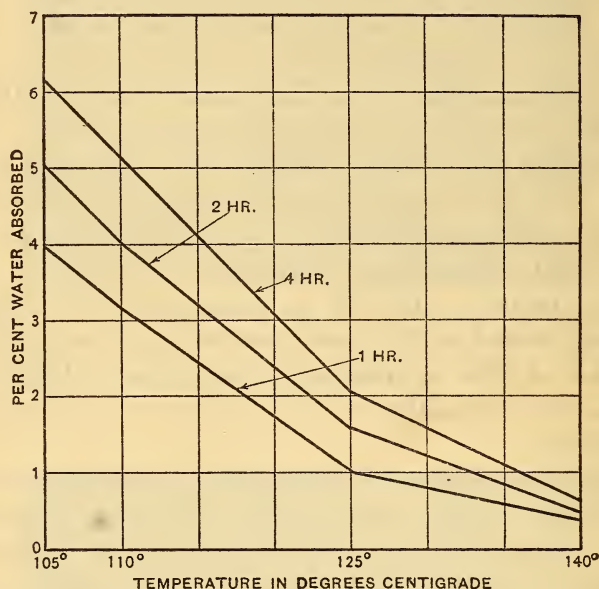


FIG. 8.—Showing the hydration of tricalcium aluminate in steam

quantities of water absorbed are given below and shown diagrammatically in Fig. 8:

	105°	110°	125°	140°
	Per cent	Per cent	Per cent	Per cent
1 hour.....	3.99	3.19	1.02	0.37
2 hours.....	5.01	4.10	1.56	.49
4 hours.....	6.21	5.19	2.12	.65

(C) *Hydration in Autoclave.*—A sample of tricalcium aluminate was stirred with an excess of water in a porcelain crucible and heated in an autoclave for two hours at 300 pounds pressure.

The microscopic examination showed that all the material had hydrated. The hydration product was chiefly amorphous but contained a few hexagonal plates as well as needles. Test of the amorphous material with anthrapurpurine and patent blue proved it to be hydrated tricalcium aluminate. There was an increase in the amount of crystals over those noted in the steamer.

(D) *Hydration of Molded Specimens*.—Mixing the material with 30 per cent of water and molding it caused the liberation of much heat and quick setting of the material, which became granular and very difficult to trowel. Examination after 24 hours showed that but a small portion of the material had hydrated. Only the edges of the grains were changed to the usual amorphous condition. The liberation of heat is interesting in view of the apparent endothermic reaction taking place when it is subjected to steam at atmospheric pressure. No explanation of this difference is made.

(E) *Composition of the Hydrated Tricalcium Aluminate*.—In an effort to determine the composition of the hydrated aluminate a 2-gram sample was shaken in a jar completely filled with 150 cc of boiled distilled water, the material being examined from time to time to determine when crystallization was complete. The addition of water resulted in the formation of lumpy, amorphous, hydrated aluminate on the outside of the grains, which had a tendency to cohere and prevent the penetration of more water. These lumps were broken up by shaking the suspension with steel shot, and in eight days all the amorphous material had been converted into fine crystals of hydrated tricalcium aluminate. The material was dried for two hours on a steam plate at 100° and the analysis gave:

	Per cent	Molecules
Al ₂ O ₃	27.52	1.0
CaO.....	45.60	3.0
H ₂ O.....	26.94	5.5

This corresponds to the formula of $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 5\frac{1}{2}\text{H}_2\text{O}$. Another portion of the material was dried in a vacuum dessicator over sulphuric acid for 48 hours, and had the composition of 3CaO .

$\text{Al}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$. The water content as determined should be considered more or less approximate, since the vapor-pressure method must be used when the highest degree of accuracy is required.

6. DIALYSIS EXPERIMENT

In an effort to ascertain whether with actual solution in a large excess of water the aluminates are hydrolyzed into calcium and aluminum hydrates, Stern's¹⁶ experiment was repeated. The apparatus, a diagram of which is given in Fig. 9, consisted of a two-hole bell jar (A) on a glass plate (B) with a ground contact

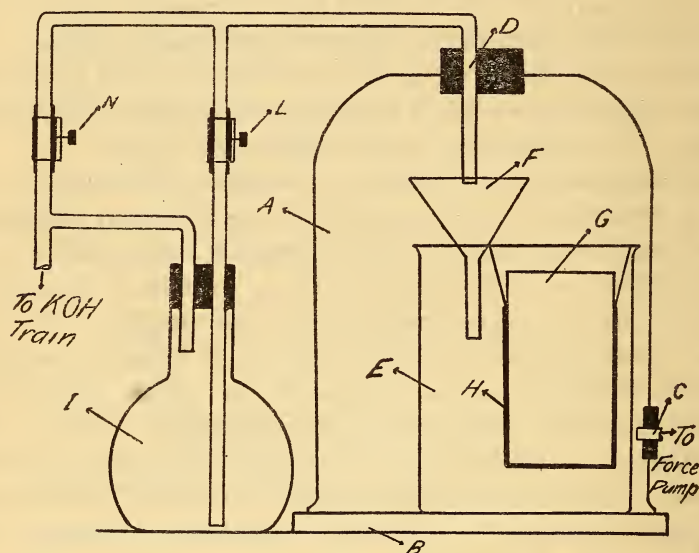


FIG. 9.—Showing filtering and dialysing apparatus

which was made air-tight. Connections were made at (C) with a vacuum pump and at (D) with the flask (I) and the potash train. Inside the jar was placed a beaker (E) containing, suspended, a funnel (F) and a piece of wide glass tubing (G), around one end of which was stretched a parchment paper (H) as dialyzing membrane. The parchment was examined carefully with a hand glass and microscope for flaws. A little tricalcium aluminate was mixed with a large excess of water in the flask (I), and the flask was shaken at intervals for ten days until a saturated solution had

¹⁶ Chem. Ztg., 32, pp. 1029-1031; 1908.

been formed. Care was taken to exclude carbon dioxide, owing to its great affinity for hydrated aluminates; but with all precautions some calcium carbonate was formed, and it was necessary to filter this together with the solid hydrated tricalcium aluminate before dialysis could be carried out. To avoid any further carbonation, it was necessary first to remove all carbon dioxide from the bell jar containing the beaker (H) and then to filter the solution into the beaker. This was accomplished in the following manner:

The necessary amount of distilled water free from carbon dioxide was placed into the dialyzing tube (G), the bell jar (A) was hermetically sealed on plate (B), and at (D) connection was made with the potash train by closing the cock (L). The cock (N) was closed, and by means of the vacuum pump the bell jar was evacuated. Then the cock on the force-pump line (not shown in diagram) was closed, and (N) was opened sufficiently to allow a steady stream of air free from carbon dioxide to enter the bell jar. This operation was repeated five times. Connection was then made through the flask by closing (N). By regulating the force pump and the cock (L) the contents of the flask was siphoned drop by drop through the filter (F) and into the beaker (E), the operation being carried out in an atmosphere entirely free from carbon dioxide.

The apparatus was allowed to stand for 11 days before the contents of the dialyzing tube (G) was analyzed. Contrary to Stern's statement, both lime and alumina were found, and in the proportion of almost 3 to 1. This tends to show that the lime and alumina, which passed through the parchment, did so as the hydrated tricalcium aluminate and that there was no hydrolytic dissociation.

7. HYDRATION OF TRICALCIUM ALUMINATE CONTAINING 5:3 CALCIUM ALUMINATE AND FREE LIME, WITH WATER

As free lime has been found by microscopic investigation to be a usual constituent of high limed cements, a sample of material, containing about 20 per cent less alumina than that required to form the tricalcium aluminate, was burned and then examined petrographically. The major portion of the material consisted of tricalcium aluminate, but a considerable amount of high-

burned free lime and a minute quantity of 5:3 calcium aluminate were also noted.

(A) *Hydration in Steam at Atmospheric Pressure.*—The most marked temperature variations of all the specimens were noted here. For instance, in hydrating a sample at 110° , it was noted that for 20 minutes after the beginning of the operation the inner thermometer showed 110 – 111° and the outer 118° . At the end of this period the inner temperature suddenly fell to 101° , and it became necessary to bring the outside temperature to 190° before the inner temperature rose to the required point. It was found

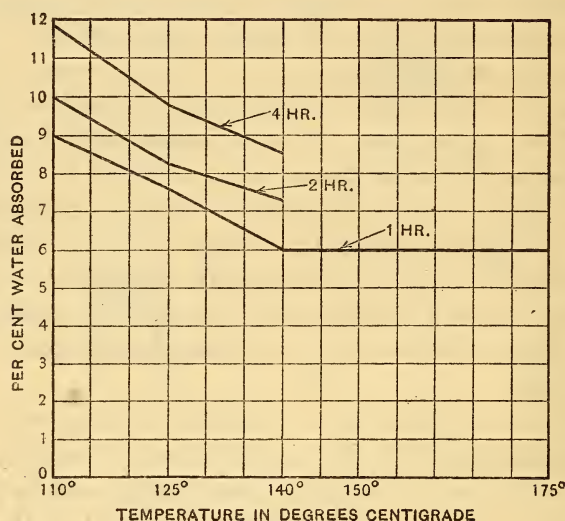


FIG. 10.—Showing the hydration of tricalcium aluminate, 5:3 calcium aluminate and lime in steam

necessary to hold the outer temperature at 190° during the rest of the period, because of this strong endothermic reaction. The hydration of this mixture of compounds at 110° for one hour showed a little unhydrated lime, amorphous lime hydrate, but no crystalline hydrate, and a small amount of hydrated tricalcium aluminate. With increase in time much larger amounts of material were hydrated, though even at the end of four hours not all the lime had been converted into hydrate. With increase in temperature the amount of hydrated material decreased. However, the lime did not cease hydrating at 175° , the limit of the test.

The quantities of water absorbed are given below and shown diagrammatically in Fig. 10.

	110°	125°	140°	150°	175°
	Per cent	Per cent	Per cent	Per cent	Per cent
1 hour.....	8.90	7.60	6.04	6.03	6.00
2 hours.....	9.91	8.29	7.20
4 hours.....	11.85	9.76	8.54

The curve of the percentage water absorption is nearly a straight line for higher temperatures, showing that the free lime was still being hydrated.

(B) *Hydration on Slide*.—Hydrated with excess of water on the slide the specimen showed crystallized hydrated tricalcium aluminate and amorphous material, some of which gave the characteristic lime phenolate crystals with White's reagent.

(C) *Hydration in Autoclave*.—A specimen hydrated in the autoclave also gave crystallized hydrated tricalcium aluminate as well as amorphous material. In addition a few incompletely developed crystals of calcium hydrate were noted.

(D) *Hydration of Molded Specimens*.—A specimen hydrated with 30 per cent water and molded into a cube, showed after 24 hours amorphous calcium hydrate, amorphous hydrated aluminate, and considerable unhydrated material, including free lime.

8. HYDRATION OF LIME

The previous results of the hydration of the aluminate mixed with free lime in steam at atmospheric pressure show that with steam acting on material passing through the 200-mesh sieve no crystalline calcium hydroxide is formed while in the autoclave with the same material hexagonal plates of hydrate are found, indicating that with increased heat and increased pressure lime is taken into solution and crystallized out. To determine whether the presence of an excess of water was responsible for this phenomena, a number of lime samples burned at various temperatures from 1200 to 1400° for one hour were exposed on slides after preliminary sifting. The sample burned at 1400° and passing the 200-mesh sieve after 48 hours hydration on the slide consisted

mainly of amorphous hydroxide with a small amount of crystalline material tending toward hexagonal development, showing birefringence but too poorly developed to permit of determination of optical constants. The material retained on the 200-mesh sieve showed considerable crystallized hydroxide in rounded to hexagonal and prismatic crystals, which grew very little in 28 day's time. Lime burned at 1300 to 1400° C—in other words, at temperatures approximating cement kiln usage—is referred to as high-burned lime. This is in contradistinction to low-burned lime, which is that burned at lime-kiln temperatures (about 1100° C).

The material burned at 1300° and retained on the 200-mesh sieve also showed considerable amounts of crystallized hydroxide, while that burned at 1200° showed mainly amorphous hydroxide with a few grains of doubly refracting material. Furthermore, a slide consisting of a commercial high calcium lime in water showed only amorphous calcium hydroxide. This indicates clearly that the burning temperature and the fineness of grain are controlling factors in determining whether the hydrated product will be amorphous or crystalline. Given the same fineness with decreasing burning temperature, the rate of hydration is increased so that supersaturated solutions are quickly formed and the lime precipitated in the amorphous condition, while as the burning temperature increases the lime goes more slowly into solution and forms a supersaturated solution very slowly, thus permitting crystal growth.

Further tests were made by exposing the lime burned at 1400° to water vapor. The material passing the 200-mesh sieve and that retained on it were placed for seven days on slides over water contained in a jar. At the end of this time the fine material (that passing through the 200-mesh sieve) was quite damp and soft, and consisted almost entirely of amorphous hydroxide with a few grains showing gray to white interference colors. The material retained on the sieve was quite dry, but lost 5.6 per cent on ignition and consisted mainly of small calcium hydrate crystals and a little amorphous material. According to Goldammer¹⁷ the solubility of lime hydrate decreases with rise of temperature, lime

¹⁷ Pharm. Centrallr., 26, p. 442; 1890.

having the power to form supersaturated solutions, while lime hydrate has not. We should therefore expect the hydrate in the autoclave to be unchanged, while the lime, according to its fineness, would yield crystallized or amorphous hydrate. This was found to be true at all temperatures and pressures employed.

Calcium hydroxide crystallizes as short, flaky, tubular hexagonal crystals. Twinning has never been observed, but the crystals sometimes show parallel grouping and skeletal development. Very good cleavage is observed parallel to (0001). Under the microscope they show a clear hexagonal outline when orientated perpendicular to the "c" crystallographic axis, but when resting on edge they exhibit a prismatic to an acicular structure. The double refraction is medium, the interference colors varying considerably with the thickness of the grain and its orientation. Some of the hydroxide crystals are thick enough to show third and fourth order interference colors. The indices of refraction are as follows: $\mu_o = 1.581 \pm 0.002$, $\mu_e = 1.557 \pm 0.002$. $\mu_o - \mu_e$ measured on a grain orientated parallel to "c" axis $= 0.023 \pm 0.003$. The interference figure is uniaxial and the optical character is negative. Lime hydrate resembles hydrated tricalcium aluminate very closely, but is differentiated by the fact that the crystals of the former are invariably larger and have a higher index of refraction. A form of lime hydrate crystallizing in the orthorhombic system has been mentioned by Glinka¹⁸ but this was not observed.

9. ALUMINATES HYDRATED IN CALCIUM HYDROXIDE, $\text{Ca}(\text{OH})_2$

In determining the effect of calcium hydroxide on the aluminates, no tests in steam at atmospheric pressure were made because of the poor crystal development obtained by steam on the aluminates alone. Molded specimens of the aluminates were hydrated for various lengths of time and other samples were heated in the autoclave up to 300 pounds. Furthermore, slides were made of the various aluminates hydrating in saturated hydroxide solutions. In every case the resultant products were examined microscopically.

(A) *Hydration on Slides.*—The hydration on slides showed the same products as those observed on slides with distilled water.

¹⁸ Bull. Soc. fr. Min. 110, p. 63; 1887.

Tricalcium aluminate hydrated as such without the formation of amorphous material. 5:3 calcium aluminate split off hydrated alumina and formed needles, plates, and spherulites of hydrated tricalcium aluminate. Monocalcium aluminate acted the same way, but split off more alumina. No new type of crystals which might indicate hydrated tetracalcium aluminate was observed.

(B) *Hydration of Molded Specimens*.—A number of specimens were mixed with 30 per cent of water, placed in molds and allowed to harden under a damp cloth for 24 hours. At the end of this time they were removed from the molds and stored for seven days in tightly stoppered bottles, some filled with distilled water, others with limewater. In the specimen of monocalcium aluminate in water the microscopical examination showed much amorphous material, a few grains still unhydrated, and a considerable number of hydrated tricalcium aluminate needles. In the specimen hydrated in limewater, there were more needles observed than in pure water, indicating an action between the hydrated alumina split off and the calcium hydroxide of the solution. Gmelin¹⁰ states that hydrated alumina absorbs calcium hydroxide forming with it an insoluble combination.

The specimen of 5:3 calcium aluminate hydrated in water and in limewater showed no difference in hydration.

The tricalcium aluminate specimens contained fewer needles in both water and hydrate solution than either of the other two aluminates. At the same time their ignition losses were higher. This is due to the fact that at the moment of hydration a dense amorphous material was formed which held its water tenaciously and did not give it up at 100°. The specimen hydrated in limewater contained still unhydrated grains at the end of seven days, and in addition a few small hexagonal plates and needles were found. The same compound kept in water also contained unhydrated grains at the end of seven days.

Another set of specimens was mixed with 5 per cent of dry calcium hydroxide and with 30 per cent of water, stored for 24 hours under a damp cloth and then placed in water and limewater, for 28 days. The monocalcium aluminate specimen showed at the

¹⁰ Handbook of Chemistry, III, p. 327; 1849.

end of this period no unhydrated material, considerable amorphous material and small needles, spherulites, and plates of hydrated tricalcium aluminate, while the specimen hydrated in lime hydrate solution showed a better needle development. The 5:3 calcium aluminate specimens showed no visible difference in the two solutions. No unhydrated material was present. The tricalcium aluminate specimens likewise showed amorphous material, needles, and plates. The period from 7 to 28 days was therefore sufficient to hydrate all the material and cause an increase in the number and size of the hydrated tricalcium aluminate crystals.

According to Le Chatelier²⁰ and Read,²¹ a tetracalcium aluminate was obtained by hydrating cement with limewater, but in no case did the addition of calcium hydroxide in any way change the composition or the character of the crystalline hydration products.

In addition, a 2-gram sample of tricalcium aluminate was shaken for 10 days in a closed flask with calcium hydroxide solution until all the material had been converted from the amorphous to the crystalline state. The suspension was then filtered, washed with alcohol, and dried in a dessicator over sulphuric acid for 24 hours, and the analysis of the residue gave a compound of the formula $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 10\frac{1}{2}\text{H}_2\text{O}$.

(C) *Hydration in the Autoclave.*—The various aluminates hydrated with an excess of limewater in the autoclave for two hours at 300 pounds pressure gave products which in no way differed from those obtained in the autoclave with water. The chief distinction noted was in the greater amount of plate crystals formed.

These hexagonal crystals were peculiar in that frequently only three sides of the hexagon were present, the rest of the crystal being irregularly shaped. The aluminates were in every case completely hydrated after two hours, there being no grains present with unhydrated centers and hydrated edges.

In the autoclave the addition of calcium hydroxide in dry powder decidedly retarded the crystal growth of the aluminates. This was particularly noticeable in the specimens of 5:3 calcium aluminate in which, with 1 per cent dry hydroxide, small plates were noted;

²⁰ J. Soc. Chem. Ind., 3, pp. 485-486; 1884.

²¹ Ibid. 29, p. 735; 1910.

with 10 per cent hydroxide these had disappeared, and with 50 per cent hydroxide only amorphous material was observed. With the trialuminate the effect was manifested in a retarding action on the hydration. With 1 per cent hydroxide, a little unhydrated aluminate and quite a few crystals were noted. With 10 per cent hydroxide considerable unhydrated aluminate was present, together with amorphous hydrate, though a few crystals were observed. With 50 per cent the amount of hydrated material had decreased, and the crystals had almost completely disappeared.²²

10. ALUMINATES HYDRATED WITH CALCIUM SULPHATE (CaSO_4)

With the addition of plaster of Paris ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$) to the aluminates all the various hypotheses concerned in the setting of cement become involved. The field is very broad and requires that consideration be given to all the salt solutions used to accelerate and retard setting. Since this investigation deals only with the hydration of cement, the problem is confined to the changes taking place in the aluminates with the addition of plaster, this being an almost universal constituent of Portland cement.

(A) *Hydration of Molded Specimens.*—Tests were made by mixing the specimens with calcium sulphate solutions of various known strengths. The first effect noted was the prevention of the evolution of any considerable amount of heat. This was particularly noticeable in the case of tricalcium aluminate, which, on mixing with 25–30 per cent of water, evolved sufficient heat to drive off part of the water as steam. This specimen was particularly examined for the presence of free lime. Its absence showed that the heat evolved was entirely due to the combination of water with the aluminate. Amorphous material was formed which was granular and had little cohesion. With the specimens hydrated in calcium sulphate solution the amorphous material was still formed, but at a slower rate, and the heat evolution was much lessened. To determine the effect of calcium sulphate solution on the extent of hydration, a number of samples were mixed with 30 per cent calcium sulphate solutions of known strengths. These were allowed to harden for 24 hours, then stored in water for 6

²² Ninth Ann. Trans. Nat. Assoc. Lime Mfrs., pp. 16–25; 1911.

days, and dried for 2 hours at 100°. The ignition losses were as follows:

Strength of calcium sulphate solution	0.01 per cent	0.05 per cent	0.1 per cent	Saturated solution
	Per cent	Per cent	Per cent	Per cent
Monocalcium aluminate.....	29.20	28.90	28.18	30.12
5:3 calcium aluminate.....	27.38	27.86	26.78	28.84
Tricalcium aluminate.....	24.50	25.06	23.06	27.28

It is noticeable that the 0.1 per cent solution gave the lowest results in each case, and this effect will be referred to later in connection with setting time. The saturated solutions gave the highest ignition losses. It is believed that the slower rate of hydration which occurs with the saturated solution permits greater penetration of water toward the center of each grain. Microscopic observations have shown that hydration takes place first around the edges of each grain and slowly proceeds toward the center. Thus in the case of the aluminates, containing no plaster, the amorphous gelatinous mass is formed instantly around each grain, preventing the ready penetration of water. Plaster, therefore, tends to keep the pores of amorphous material open.

It is very interesting to note that with monocalcium aluminate, after seven days' hydration, only that specimen hydrated in saturated calcium sulphate solution showed complete hydration, while those hydrated in weaker solutions showed unhydrated cores surrounded by hydrated material. In the case of 5:3 calcium aluminate at the end of seven days there was still a small amount of unhydrated material. The saturated calcium sulphate solution, however, gave the best crystal development. With tricalcium aluminate the above was likewise true, both amorphous and crystalline hydrated tricalcium aluminate being present. The reason for the presence of unhydrated material in the last two aluminates and not in monocalcium aluminate is due to the fact that amorphous hydrated alumina is present in the monocalcium aluminate specimens, a less amount in 5:3 calcium aluminate, and none in the tricalcium aluminate. This material coagulates very slowly, allowing a ready penetration of water, and, therefore, a correspond-

ing greater hydration. At the same time it dries out to a hard dense mass, the monocalcium aluminate giving very strong specimens as compared with the other two. In all the above specimens minute crystallites of a new compound, calcium sulphoaluminate, were noted.

(B) *Theories Concerning Retardation of Initial Set by the Use of Plaster.*—The effect of variation in the per cent of plaster above

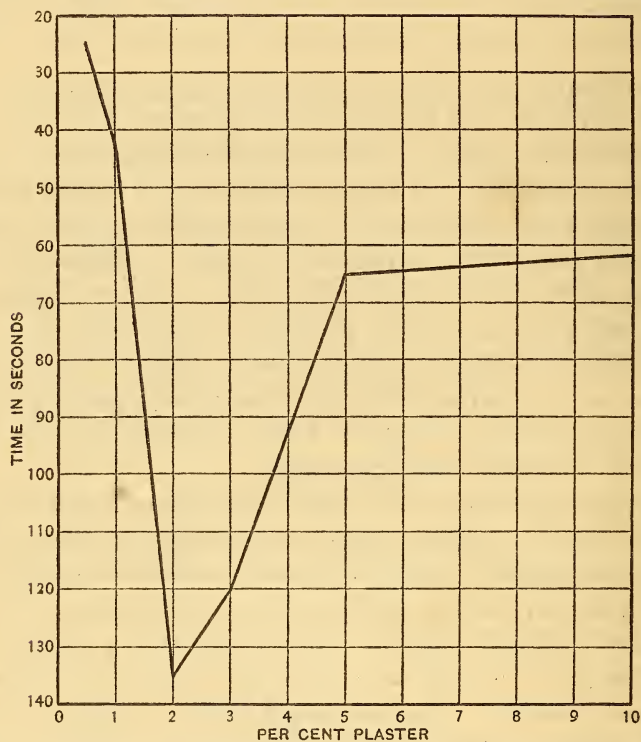


FIG. 11.—Showing the per cent plaster—time of set curve for tricalcium aluminate

or below a certain definite concentration, causing a decrease in the setting time, has been noted by Rohland²³ and other observers.

The fact that a minimum and a maximum concentration of calcium sulphate gives a rapid set and an intermediate concentration a slow set (see Fig. 11) seems to disprove Reibling's theory²⁴ that as plaster dissolves, it ionizes and reduces the solubility of other

²³ Stahl und Eisen, 28, pp. 1815-1819; 1908.

²⁴ Philippine J. Science, 6 (3), p. 210; 1911.

calcium ions already present, causing free lime to be less rapidly dissolved, the hydration of the aluminate to take place more slowly, and the setting to be retarded. If this were the case, then increasing amounts of plaster should give a correspondingly slower set, on account of the continued decrease in the solution of other lime ions already present.

The sulphoaluminate theory does not suffice to explain the retardation of the setting of cements. In observing the behavior of the above specimens under the microscope, no selective action with the water present could be noted. The aluminate began at once to hydrate, and at the same time sulphoaluminate needles were formed, their quantity steadily increasing from the beginning to the end of the initial set. However, their number at any time was very small, and, increasing the amount of plaster, though increasing the amount of sulphoaluminate needles, did not retard the set. Furthermore, the formation of sulphoaluminate needles is not sufficient to account for the retarding action of salts, such as calcium chloride, sodium borate, potassium bichromate, sugar, or other carbohydrates, which, so far as is known, do not form insoluble compounds with aluminates at the concentration used.

The problem of the retardation of the setting of cement appears to be one involving the action of electrolytes carrying positive or negative charges. This field has been investigated by colloid chemists and is treated in a general way by authors on colloid chemistry, i. e., Freundlich,²⁵ Ostwald,²⁶ Pöschl,²⁷ etc. Rohland²⁸ has attempted to apply the general principles to the particular case of Portland cement. Although the action of electrolytes offers the best explanation so far found, nothing has been definitely proven, and much more work must be done on the problem.

In referring to setting as a problem dealing with the action of electrolytes, there seems to be an analogy with the results obtained by the Ceramic Division of the Bureau in using the process for

²⁵ Kapillarchemie, 1909; Die Einwirkung der Elektrolyte auf Suspensionkolloide, pp. 345-364; Einfluss der Elektrolyte auf grobe Suspensionen, pp. 365-368.

²⁶ Grundriss der Kolloidchemie, pp. 467-505; 1910.

²⁷ The Chemistry of Colloids, pp. 14-17; 1910.

²⁸ Zs. Angew. Chem., 16, pp. 1049-1055, 1903; Tonind. Ztg., 28, p. 77, 1904; Chem. Ztg., 30, pp. 1173-1174, 1906; Zs. Chem. Ind. Kolloide, 8, pp. 251-253, 1911.

thinning clay slips by means of electrolytes. In this process extremely small quantities of an electrolyte are added to a clay slip. At definite concentrations of electrolytes in the slip there are points of maximum and minimum viscosity. At the point of minimum viscosity the less finely dispersed matter settles out fairly rapidly, while the finely divided material stays in suspension. By increasing or decreasing the concentration of electrolytes complete coagulation results. The curve is of the same general nature as that shown for the per cent of plaster-time curve for tricalcium aluminate. It is evident here that with 2 per cent plaster the amorphous material formed by the addition of water can least readily coagulate and separate as a solid from the semiliquid mass, while at another concentration of plaster the conditions for coagulation are more favorable and the separation of a solid mass occurs in a shorter time.

McKenna ²⁹ has called attention to the fact that the amorphous material separates in at least two stages, normal cements showing at about the third hour a relaxation of the first stiffening, followed by a resumption of the hardening. The explanation given is that the break indicates the separation of a compound from supersaturated solution and softening of the amorphous mass by the freed water. Later by absorption of water hardening proceeds. Bleininger ³⁰ likewise states that the conductivity of a paste of cement and water increases enormously at the time of initial set, which is in favor of a supersaturation theory.

The evidence, therefore, is in favor of the fact that the aluminates coagulate and separate as amorphous bodies from a supersaturated solution, the rate of coagulation being affected by such small quantities of electrolytes as to preclude the possibility of the reaction being solely a chemical one. The evidence points further to the fact that with a certain and definite concentration of gypsum maximum hydration is attained, at the same time the rate of coagulation is reduced to a minimum, and the time of set is lengthened.

(C) *Calcium Sulphoaluminate Hydrated*.—An interesting feature of these microscopic examinations was the isolation and identifica-

²⁹ J. Ind. Eng. Chem., 4, pp. 110-114; February, 1912.

³⁰ Hydraulic Cements, p. 341; 1904.

tion of calcium sulphoaluminate crystals. An increase in the amount of plaster showed a steady increase in the amounts of sulphoaluminate crystals, and above 3 per cent plaster a constantly increasing amount of gypsum crystals was noted. The extension of these tests to 28 days resulted chiefly in an increase in the amount and size of the hydrated tricalcium aluminate plates, no amorphous material except hydrated alumina (in the case of the 5:3 calcium aluminate and the monocalcium aluminate) being present at the end of this period. It was also noted that the sulphoaluminate needles could be found only in the undried specimens, since drying at 100° resulted in the formation of hydrated tricalcium aluminate and peculiar club-shaped crystals of calcium sulphate differing in their optical properties from normal gypsum. The optical constants pointed to a compound having a composition somewhere between that of anhydrite and gypsum.

To study further the composition of sulphoaluminate, a sample of tricalcium aluminate was shaken with water and rapidly filtered into a clear saturated calcium sulphate solution. At the end of one-half hour there was a faint cloudiness in the solution which persisted for several days, and finally a few flakes or scales were deposited on the side of the containing vessel. As they were very few in number, a solution of lime hydrate was added, and immediately a white, apparently gelatinous, precipitate formed, which on microscopical examination proved to be homogeneous and consisted of minute prismatic crystals.

In order to increase their size the solution was allowed to evaporate spontaneously in a vacuum desiccator over concentrated sulphuric acid until the solution was reduced to about one-third of its original bulk. It was then rapidly filtered, washed with lime hydrate solution, alcohol, and ether, and air dried for two hours. The analysis of the crystals showed:

	Per cent com- position	Molecules
CaO.....	26.1	6.0
Al ₂ O ₃	7.8	1.0
SO ₃	19.9	3.0
H ₂ O.....	46.1	36.5

Hence the formula of the calcium sulphoaluminate crystals is $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 36\frac{1}{2}\text{H}_2\text{O}$.

Another sample was washed with limewater, alcohol, ether, and sucked dry with the filter pump. Its formula was found to be $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 42\text{H}_2\text{O}$. These needles (see Fig. 12) were identical optically with those observed by hydrating the aluminates on a slide with a saturated gypsum solution.

There is considerable variation in the water content reported by various experimenters, such as 19.5 per cent by Klinkenberg,³¹ 55.71 per cent by Candlot,³² 30 per cent by Michaelis,³³ and 28.5 per cent by Deval.³⁴

These variations in water content indicate the ease with which it loses water, all of it being lost at 100° . The unsuccessful attempts by Bates³⁵ to produce a compound of this composition were due to the fact that fused tricalcium aluminate was used. This compound contained besides tricalcium aluminate, 5:3 calcium aluminate, and free lime. The latter two compounds were formed through the partial disassociation of the tricalcium aluminate at its melting point. On treating it with water gelatinous aluminum hydroxide was formed and was filtered out with the rest of the precipitate, thus upsetting the balance of the elements in the analysis.

(D) *Hydration on Slides.*—The method followed was the same as that employed in the similar investigation with water. In this case, however, a saturated solution of calcium sulphate was used. Tricalcium aluminate began to hydrate almost immediately with the formation of needles and plates of hydrated tricalcium aluminate. Shortly, however, there began to form extremely fine needles (see Fig. 13), which were very difficult to observe and could be seen only when the cone of light from the substage of the microscope was reduced to almost vertical rays by closing the substage diaphragm. Even then they could be detected only after careful study. These needles, while always remaining long and slender, grew in size and thickness until interference colors were

³¹ Dinger's Poly. J., 249, pp. 89-95; 1894.

³² Bull. Soc. D'Encouragement, 73, pp. 685-716; 1890.

³³ Proc. Inst. Civil Eng., 107, p. 370; 1892.

³⁴ Bull. Soc. D'Encouragement, pp. 30-54; January, 1900.

³⁵ Tech. Paper, Bureau of Standards, No. 12, pp. 37-39; 1912.

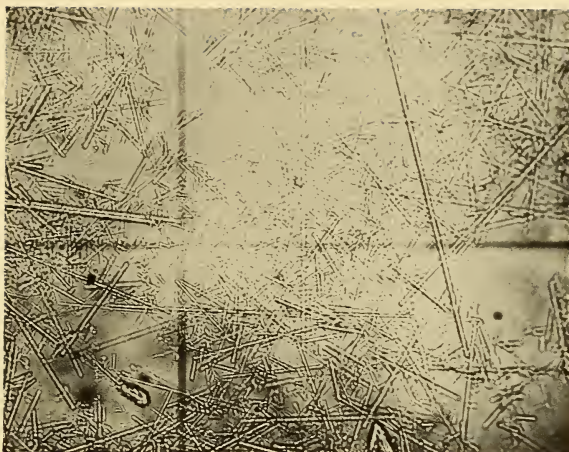


FIG. 12.—Showing long slender needles of calcium sulphoaluminate obtained by the reaction of solutions of tricalcium aluminate and calcium sulphate. This was taken without nicols and the magnification = 400 diameters

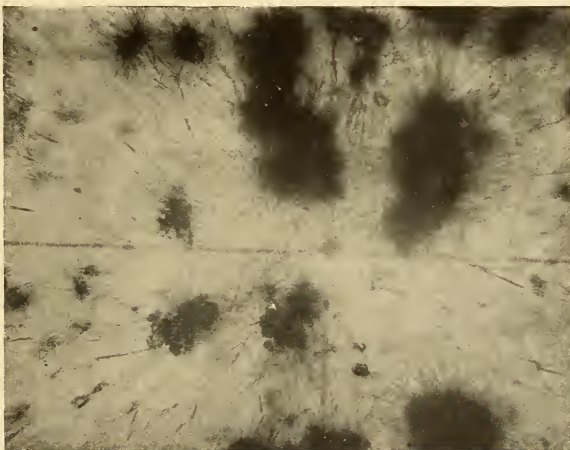


FIG. 13.—Showing fine needles of calcium sulphoaluminate observed on a slide of tricalcium aluminate hydrated in a calcium sulphate solution. This was taken without nicols, and the magnification = 280 diameters

observed with crossed nicols. The maximum color noted was white of the first order, showing a low double refraction.

In order to study more carefully the optical constants of this new compound, a slide was hydrated until apparent maximum crystal growth was attained. It was then dried in a vacuum desiccator, care being taken not to dry too long, since it was found that sulphuric acid absorbed the water of crystallization from the sulphoaluminate crystals. Generally about one hour was sufficient to dry the slide.

Microscopic observations of the sulphoaluminate crystals showed their long prismatic development. Twinning was not noted, but occasionally irregular intergrowths were observed. The crystals showed low interference colors ranging from black to white of the first order. The character of the principal zone was negative and the extinction parallel. The indices of refraction could not be obtained quantitatively, since they were lower than 1.48 (the lowest index in our series of immersing liquids). The interference figure was biaxial with a large optic axial angle. Owing to the low double refraction the interference figures showed only black bars with hazy outlines, and no color isogyres were noted. The optical character was positive. These crystals could easily be distinguished from the hydrated tricalcium aluminate crystals by their lower double refraction, different character of their principal zone, and different prismatic development, the terminations being flat, perpendicular to the long axis of the prism, and not pointed, as in the case of the hydrated tricalcium aluminate.

The 5:3 calcium aluminate slide started to hydrate very soon with the formation of amorphous material, spherulites, needles, and hexagonal plates noted in the hydration of slides with water. At the same time crystals of sulphoaluminate were formed having optical properties identical with those observed in the hydration of tricalcium aluminate in calcium sulphate solution. They were, however, larger and more easily observed. As in the previous case the specimen was dried in the desiccator and examined while immersed in liquids of known refractive indices.

The monocalcium aluminate slide hydrated in a short time and gave the same resulting products as the 5:3 calcium aluminate

slide. The amount of amorphous hydrated alumina was greater and the crystals of sulphoaluminate were better developed. The optical constants of the latter were identical with those of the sulphoaluminates observed on the tricalcium aluminate and 5:3 calcium aluminate slides, and as has been stated before, they were identical with the needle crystals obtained by the action of a solution of tricalcium aluminate on a saturated calcium sulphate solution.

Hydration on slides with mixtures of one part lime hydrate and one part calcium sulphate solution gave no new hydration products but increased the quantity of sulphoaluminate crystals.

(E) *Hydration in the Autoclave*.—No sulphoaluminate needles were observed in any specimens which were exposed to the autoclave test, and, as Kühl³⁶ has pointed out, the heat of the steam bath is sufficient to break up the compound into its component constituents. However, club-shaped crystals were noted. As had been noted before, from optical considerations these crystals have a composition between that of gypsum and that of anhydrite. They have a higher index than the former; $\alpha = 1.561 \pm 0.003$ and $\gamma = 1.577 \pm 0.003$. The crystals show parallel extinction, medium low double refraction, and interference colors of the first order. The character of the principal zone is positive, and the interference figures are biaxial.

That these club-shaped crystals are intermediate in composition between gypsum and anhydrite is shown by the fact that the index of refraction and the double refraction are both greater than that of gypsum and less than that of anhydrite. The extinction is identical with that of the latter.

Monocalcium aluminate hydrated with various amounts of plaster at 300 pounds pressure for two hours showed amorphous material, and a few hexagonal and needle crystals of hydrated tricalcium aluminate. The same was true of 5:3 calcium aluminate, which showed an increase in the content of hydrated tricalcium aluminate crystals. With tricalcium aluminate very large plates and needles of hydrated tricalcium aluminate were found.

³⁶Mitt. Zent. Ford. Deut. Port. Cement. Ind., 2, pp. 108-110; 1913.

With the aluminate containing free lime, very large crystals of calcium hydroxide were found in addition to the other products of hydration. The effect of adding hydrated lime to the plaster and aluminate was simply to increase the amount of amorphous material, no effect on crystallization being noted.

It was found that the water of hydration could likewise be partially driven out of the amorphous hydration product of the aluminates and the refractive index raised by holding the pressure at 400 pounds for four hours and maintaining the samples in an atmosphere of steam. In the other cases where the specimens were kept in water in the autoclave during the test there was still a slight rise in refractive index but not as great as before. The conditions attained were sufficient to drive out a part of the water. So the water content in any hydrated aluminate specimen is largely dependent on how it is dried.

III. SILICATES (INCLUDING MIXTURES OF SILICATES AND ALUMINATES)

1. HYDRATION OF CALCIUM METASILICATE ($\text{CaO} \cdot \text{SiO}_2$)

Calcium metasilicate was prepared like the other specimens by burning in the updraft kiln. It was found to be pseudowollastonite. It occurred in irregular intergrown grains showing no crystalline outline, had a high double refraction, white of the highest order being the maximum color observed. The refractive indices were $\alpha = 1.61 \pm 0.003$; $\gamma = 1.65 \pm 0.003$. $\gamma - \alpha = 0.04$. The biaxial interference figure was very characteristic, but in many cases it was difficult to distinguish it from a uniaxial figure, since the optic axial angle was very small. The optical character was positive. No free lime was observed in this specimen. The chemical analysis showed:

	Per cent
SiO_2	51.45
Al_2O_317
Fe_2O_308
CaO	48.16
Ignition loss.....	.18
(See Tables 2 and 3.)	

Neither in steam at atmospheric pressure nor by hydration in water did calcium metasilicate take up any water, nor was there

any hydration on a slide. By placing the material in a metal receptacle containing water and placing the whole in an autoclave for two hours at 300 pounds an extremely slight etching of the crystals was obtained, but the amount of water taken up was insignificant. All attempts to hydrate it in saturated limewater and in saturated calcium sulphate solution on slides gave negative results. The examination of slides containing mixtures of the silicate with each of the three aluminates in water, limewater, and calcium sulphate solutions showed that the silicate did not hydrate, but that the aluminate gave the same hydration products as when they alone were hydrated in these solutions.

2. HYDRATION OF GAMMA-CALCIUM ORTHOSILICATE ($\gamma 2\text{CaO} \cdot \text{SiO}_2$)

Gamma-calcium orthosilicate was very readily prepared by mixing the materials in proper proportion and burning in a pot furnace. The specimen was then removed from the furnace while red hot and allowed to dust down in the open air. Much dusted material passed readily through the 200-mesh sieve without any further grinding. The gamma-orthosilicate as prepared consisted of very small prismatic crystals with a fair cleavage parallel to the prism axis. The cleavage, however, was not very generally observed. No twinning was noticed. The refractive indices were: $\alpha = 1.641 \pm 0.002$, $\beta = 1.645 \pm 0.003$, $\gamma = 1.655 \pm 0.002$. The interference colors were generally white to yellow of the first order. Double refraction (measured) = 0.015 ± 0.003 . The extinction was parallel in most cases; sometimes, however, inclined extinction was observed, the maximum angle being about 3° . Biaxial interference figures were observed with the angle of the optic axis perpendicular to the prism axis. The optical character was positive. The chemical analysis showed:

	Per cent.
SiO ₂	34.58
Al ₂ O ₃60
Fe ₂ O ₃16
CaO.....	64.63
Ignition loss.....	.07

By heating the silicate in steam at atmospheric pressure at 110° for four hours, 0.52 per cent of water was taken up. Micro-

scopically the material was but slightly altered. A little etching on the edge of some of the grains was observed, and a few small doubly refracting grains of lower index were noted, but they were too minute for further identification. Attempts to hydrate the material in water or in the autoclave gave similar results, extremely small amounts of water being fixed. Hydrated on a slide with water, limewater, or gypsum, it likewise showed no change. No hydration of this silicate was noted on mixing it with any of the aluminates, with plaster, or with limewater and storing in water.

3. HYDRATION OF BETA-CALCIUM ORTHOSILICATE (β - $2\text{CaO} \cdot \text{SiO}_2$)

(A) *Preparation*.—True to the reports of previous investigators, great difficulty was encountered in preparing this compound. It was not possible to secure temperatures in the kiln much over $1,500^\circ$, and this temperature was not sufficient to prevent dusting of the material when taken from the kiln, even after plunging it under water or under mercury. By burning in a pot furnace, a higher temperature was reached, but considerable quantities of magnesia were found in the beta-calcium orthosilicate thus prepared. In some cases the specimens were colored brown due to iron. These contaminations resulted from the volatilization of magnesia and ferric oxide in the magnesite brick. Finally, recourse was had to an electrical resistance furnace of the type used by the Ceramic Division of the Bureau for determination of melting points (see Fig. 14).

The magnesite plug at the bottom supported the specimen within the hot zone. By this means the specimens could be rapidly withdrawn from the furnace and plunged into water or mercury. This, however, was found to be unnecessary, since no tendency toward dusting was noted on removal of the material from the hot furnace. It should be noted also that small amounts of magnesia were added to prevent dusting. Considerable difficulty was found with the refractory lining used, as it cracked under conditions of rapid heating and rapid cooling to which it was subjected. Fused magnesia with magnesium chloride, alundum, ground magnesite brick, magnesia with alumina, and magnesia

with feldspar were tried. The most satisfactory mixture consisted of thirty parts of feldspar and seventy parts of magnesia, intimately mixed, ground, molded with water, and given a preliminary firing in the pot furnace. This lining showed no tendency

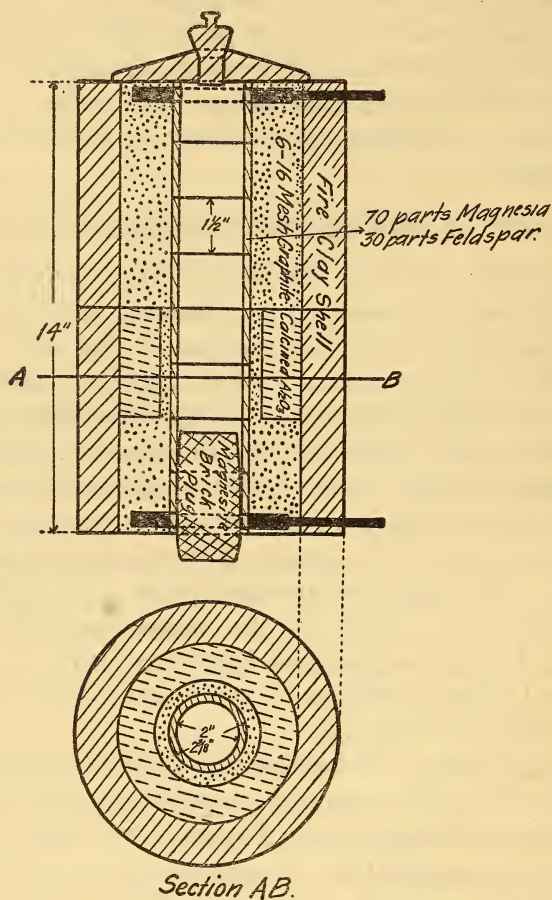


FIG. 14.—Showing carbon resistance furnace

toward cracking, but under the severest conditions they grew a little soft, during a prolonged run.

The beta-calcium orthosilicate prepared consisted chiefly of overlapping grains, some without definite outline and some showing prismatic development. No twinning was observed. Cleavage was noted parallel to the prism axis, and extinction was parallel.

The refractive indices were $\alpha = 1.720 \pm 0.003$, $\gamma = 1.735 \pm 0.003$. Maximum interference color observed was yellow of the second order. Biaxial interference figure was noted with a large optic axial angle. The chemical analysis showed:

	Per cent.
SiO ₂	35.21
Al ₂ O ₃56
Fe ₂ O ₃21
CaO.....	63.53
MgO.....	.37
Ignition loss.....	.22

The fact that magnesia prevents dusting of the orthosilicate was noted by Le Chatelier,³⁷ Sefetrom,³⁸ and by this laboratory³⁹ in their work on magnesia in Portland cement. A very small amount was sufficient to accomplish this, although the burning temperature was found to be a great factor. No beneficial action was noted from the presence of magnesia when the specimens were burned in the pot furnace at 1500° C.

(B) *Hydration in Steam at Atmospheric Pressure and in Autoclave*.—Unexpected difficulties were met in attempting to hydrate beta-orthosilicate as it appeared extremely reluctant to take up water. Heating it in steam at temperatures from 105 to 140° caused no water absorption and no visible change in the material. Likewise there was no hydration when it was allowed to stand with an excess of water except after a considerable length of time when there was an extremely slight hydration. On exposing the material to both steam and hot water in the autoclave, only a slight etching of the crystal edges and formation of a little isotropic hydrated material was noted.

(C) *Hydration on Slide with Water*.—Beta-orthosilicate mixed with a large excess of water on a slide underwent no change until after six weeks, when a very slight etching of some of the grains was noted, and a slight amount of isotropic hydrated material was observed.

(D) *Hydration with Calcium Hydroxide*.—Only a slight action on the beta-orthosilicate was noted when it was hydrated with lime hydrate solution for seven days. Grinding with high-

³⁷ Ann. Mines, 170, pp. 383-412; 1887.

³⁸ J. für Tech. u. Okonom. Chemie., 10, p. 145; 1831.

³⁹ Orig. Com., 8th Int. Cong. Applied Chem., 5, pp. 73-81; 1912.

burned lime and then adding water did not increase the hydration. The silicate crystals in both cases were etched especially along the edges, where the refraction was lowered and a slight amount of amorphous material formed. The same results were obtained in the autoclave, only to a greater extent.

Continuing the tests to 28 days, samples of beta-orthosilicate were gauged with limewater and molded into small cylinders. After 24 hours these were removed from the molds and immersed in water for 27 days. At the end of this time the specimens were soft, friable, and consisted almost entirely of unchanged silicate surrounded by a thin layer of amorphous hydrated material. Continuing the tests to 90 days the hydration became more marked. Nevertheless, there remained considerable unhydrated silicate even at this period.

The inability to hydrate beta-orthosilicate prevented the determination of the temperatures above which it loses water. Bied states that this temperature for the basic silicates is 140° , while Ljamin⁴⁰ states that the bound water of the silicate is lost at 150° .

Burian and Seber,⁴¹ who studied the hydrolysis of cements by conductivity measurements, found that hydration took place much more rapidly in limewater than in distilled water. However, at best there were observed only a small increase with lime-water. Probably the small amounts of other materials in cement, such as alkali and ferric oxide, play some part.

Very conflicting results are reported as to the hardening of beta-orthosilicate with water. Le Chatelier⁴² found that neither water nor limewater had any effect on it. Bied⁴³ has noted the inertness of beta-orthosilicate toward hydration. He baked tablets of this composition containing 2-3 per cent R_2O_3 to $1600-1700^{\circ}$, ground the specimens, mixed them with water, and stored them under water for one year. At the end of this time they had no appreciable strength. Richardson⁴⁴ thought it had little hydraulicity except in the presence of carbon dioxide and while

⁴⁰ Protocol, German Port. Cement Mfrs. Assoc., p. 52; 1898.

⁴¹ Chem. Listy, 6, pp. 145-149; 1912.

⁴² Ann. Mines, 170, pp. 388-412; 1887.

⁴³ Proc. Int. Assoc. Mat. 2, (9), p. 8; 1911.

⁴⁴ Cement, 5, p. 117; 1905.

setting slowly in water was not volume constant. Newberry⁴⁵ states that the silicate set hard in 7 days and boiled sound, and whether fused or not it maintained its previous composition and lost very little lime. Schott⁴⁶ made a product that set in 24 hours and hardened well in 8 days. Unger⁴⁷ found that his stable material after mixing with water gave a strength of 140 pounds in 8 weeks, part of this being due to carbonation from carbon dioxide in the air. It is interesting to note that as early as 1865 Heldt⁴⁸ was able to obtain hardening mixtures from lime and alkali silicates, Oddo⁴⁹ likewise agreed with Le Chatelier in being unable to prepare a product which would harden with water.

(E) *Hydration with Calcium Sulphate Solution.*—Mixing the silicate with a saturated solution obtained from plaster gave no appreciable hydration, and treatment in the autoclave resulted only in the previously noted change in the gypsum.

(F) *Hydration with a Large Excess of Solution.*—As it is generally considered that a large excess of water hastens the hydration of cement, the effects of an excess of solution on the beta-orthosilicate were studied. Efforts were made to hasten its hydration by placing 1-gram samples in tall glass-stoppered cylinders, to which were added 150 cc of one of the following liquids: Water, saturated tricalcium aluminate solution, saturated limewater, saturated calcium sulphate solution, a solution made by shaking freshly precipitated and well-washed aluminum hydrate with a large excess of water and filtering, and a 2 per cent solution of aluminum sulphate. The cylinders were well shaken and rotated in a slow-moving stirring apparatus for 10 days. At the end of the second day there was noted with the tricalcium aluminate solution a slight permanent suspension in the cylinder, while the others settled out to a precipitate and a perfectly clear solution in less than a minute. At the end of the tenth day a very large amount of permanently suspended material was noted in the tricalcium aluminate solution, while the limewater and the calcium sulphate, etc., solutions contained only a little flocculent material in addition to the precipitate.

⁴⁵ Bull. Soc. D'Encouragement, 99, p. 647; 1903.

⁴⁶ Cement Eng. News, 22, p. 287; 1910.

⁴⁷ Cement Eng. News, 22, p. 287; 1910.

⁴⁸ J. Prakt. Chem., 94, p. 129; 1865.

⁴⁹ Accad. dei Lincei, 26, p. 361; 1896.

After drying, the product was examined microscopically. The material treated with the aluminate solution still contained some unhydrated beta-orthosilicate and a considerable amount of the isotropic amorphous material. The silicate hydrated in the other solutions showed considerably less hydration in the following decreasing order: Calcium sulphate, limewater, aluminum sulphate, hydrated alumina, and water. The products of hydration were identical in each case and consisted of amorphous material. No calcium hydroxide was present.

After washing and drying all the treated specimens for two hours at 100° the ignition losses were as follows:

	Per cent.
Tricalcium aluminate solution.....	4.04
Plaster solution.....	1.94
Lime hydrate solution.....	1.73
Aluminum sulphate solution.....	1.38
Aluminum hydrate solution.....	1.04
Water.....	0.97

(G) *Inversion of Beta-Orthosilicate to Gamma-Orthosilicate.*—It must be noted that beta-orthosilicate, after being given a steam treatment and dried on the hot plate for the determination of the water, showed considerable amounts of the gamma form. This effect was also noted in the material ground to about six-mesh size and stored in bottles. There was a slow accumulation of powder at the bottom of the bottles which proved to be gamma-orthosilicate. The rate of its formation, however, was not constant, the largest amounts being formed within two or three days after the burning of the specimen. Further dusting proceeded slowly. It is evident that heat accelerates this change, and, furthermore, it is found that dusting proceeds more quickly in specimens where the beta-orthosilicate is very fine grained. In specimens containing larger crystals, due evidently to prolonged heat treatment, there was not the slightest evidence of dusting even at the end of three months.

4. HYDRATION OF BETA-CALCIUM ORTHOSILICATE AND ALUMINATES

(A) *Hydration in Steam at Atmospheric Pressure.*—To observe any possible action of the aluminates on beta-orthosilicate at atmospheric pressures, mixtures of 70 parts of silicate and 30

parts of aluminates were first ground together and then treated with steam at temperatures up to 140° . Microscopical examination showed that the aluminate alone had been hydrated. These tests were made with each of the three aluminates. To insure better contact of the material the mixtures of silicate and aluminate were placed in small linen bags which were then sewed up and treated with steam with like results.

It was realized that even with the very finest grinding of the mixture the intimate contact of aluminate with silicate in a cement could not be reproduced. Therefore, a number of cements were heated in steam for as long as four hours at temperatures ranging from 105° to 140° . In every case the amount of water absorbed was from 3 to 6 per cent, and in no case was the beta-orthosilicate hydrated.

(B) *Hydration in the Autoclave.*—Corresponding tests in the autoclave showed a slight etching of the silicate crystallites with the usual hydration of the aluminates. A mixture hydrated in an excess of water for 24 hours then placed in the autoclave showed no more hydration than that noted in the autoclave alone.

(C) *Hydration of Molded Specimens.*—Mixtures of beta-orthosilicate with monocalcium aluminate, 5:3 calcium aluminate, and tricalcium aluminate, respectively, and a small amount of plaster were hydrated in limewater and in water for 28 days. A slight increase in the amount of hydrated material was noted with limewater over that with water. The specimens were somewhat friable but stronger than the 28-day hydration specimen of the beta-orthosilicate hydrated in a solution of tricalcium aluminate. One peculiarity was noted in that on the outside of the specimens glistening crystals were seen, which in some cases could be picked off with the forceps. Microscopical investigation proved these to be hydrated tricalcium aluminate. In addition there were a few calcium carbonate crystals resulting from the decomposition of the aluminates by the carbon dioxide in water. Very few small crystals were noted when the specimens were broken open. The indications are that there was a diffusion of aluminate from the interior to the surface followed by crystallization.

(D) *Hydration on Slides.*—In this series mixtures were made of about three parts of beta-orthosilicate to one part of each of the

following: Tricalcium aluminate, 5:3 calcium aluminate, and monocalcium aluminate. This ratio was used to conform to the approximate quantitative relationship of the above compounds in a Portland cement. The same procedure was followed as with all previous hydrations on slides.

With beta-orthosilicate and tricalcium aluminate the first effect noted was the immediate beginning of hydration of the aluminate. This, when hydrated, formed needles and plates of hydrated tricalcium aluminate, similar to those previously observed. At the end of two days the silicate showed signs of being etched, and a little amorphous material was noted along the edges of the silicate grains. The etching continued and at the end of a week the amorphous material was fast surrounding the silicate crystallites. At three weeks practically the whole slide was covered with amorphous material; but the aluminate needles and plates were unchanged, although their definiteness of outline was often obscured by the amorphous silicate material. (See Fig. 15.) No calcium hydroxide crystals were observed. A slide dried in an atmosphere free from carbon dioxide and treated with White's solution showed the absence of amorphous calcium hydroxide.

None of the crystallized needles of hydrated silicate noted by previous investigators, Kaisermann,⁵⁰ for instance, were observed. Recourse was had to a paraboloid condenser for dark field illumination, which Kaisermann states was necessary for the observation of these needles. Again nothing was observed but amorphous material, having no definite crystalline outline whatsoever. Furthermore, according to Kaisermann, an excess of water prevented the formation of these needle crystals, and insufficient water caused the preparation to dry before there was opportunity for crystallization. Under the assumption that too much or perhaps too little water was used in the preparation, a series of five slides were made up with varying amounts of water. In every case the hydration products were the same as previously noted. In no case were there any fine needle crystals of silicate observed. Needles of hydrated tricalcium aluminate were of course noted; but they could not be confused with the silicate

⁵⁰ *Cement and Eng. News*, 23, p. 62; 1911.

needles, for, according to Kaisermann, the latter have a different crystal development and show almost no double refraction.

Michaelis⁵¹ in commenting on the needles of lime silicate observed by Kaisermann, states that the latter did not prove their composition and that they may be zeolite, gypsum, or sulphoaluminate crystals. The fact that Kaisermann observed these crystals in mixtures supposedly made from lime and silica would probably preclude the possibility of their being either gypsum or sulphoaluminate crystals. On the other hand, he states they were more readily observed in puzzolana cements. Puzzolana cements, puzzolana, trass, tufa, etc., contain soluble silica which combines with lime. In addition, they contain zeolites which exchange their base for lime on coming in contact with the latter. So it seems possible that the crystals observed were formed by the presence of impurities in the silica used.

A slide of beta-orthosilicate and tricalcium aluminate was dried in an atmosphere free from carbon dioxide after the hydration was apparently completed. It was then hydrated again on a slide with more water. The hydrated silicate again showed no needle development, but occurred in amorphous round grains. No splitting off of calcium hydroxide was observed.

The first effect of the hydration of beta-orthosilicate and 5:3 calcium aluminate was the formation of radial spherulites and the subsequent growth of needles and plates of hydrated tricalcium aluminate, together with the formation of some amorphous material. The silicate started to hydrate within two days with the formation of amorphous gelatinous material, which at the end of 16 days covered the whole slide. No calcium hydroxide was observed in any form and no needle crystals of hydrated silicate were noted. Similar slides were also prepared with varying amounts of water, and observations were made with dark field illumination, but no silicate needles were found. No hydration product of the silicate was observed which possessed even the slightest double refraction.

The slides of monocalcium aluminate and beta-orthosilicate behaved much like those of the preceding series. The aluminate

⁵¹ *Cement and Eng. News*, 23, p. 57; 1911.

hydrated first with the splitting off of considerable hydrated alumina and the formation of needles, plates, and spherulites of hydrated tricalcium aluminate. The silicate commenced to hydrate in a couple of days to the previously observed amorphous material, which at the end of a week covered the whole slide and was so thick as to preclude further observation.

No reason for the behavior of the aluminates in hastening the hydration of the beta-orthosilicate has been found, other than that it is simply a case of the silicate being more soluble in the aluminate solution than in water, and that a saturated solution is formed with subsequent precipitation of the amorphous hydrated silicate.

5. HYDRATION OF TRICALCIUM SILICATE ($3\text{CaO} \cdot \text{SiO}_2$)

(A) *Preparation.*—Tricalcium silicate was prepared by mixing calcium carbonate, to which a small amount of magnesia had been added, and silica in the proper proportion with water, and molding the mixture into hollow cylinders. These were dried and burned in a pot furnace at 1500°C . The specimens were then withdrawn from the furnace and allowed to dust down. The coarser particles of the resultant product were ground until all the material passed the 200-mesh sieve. The powder was then remolded with a dilute sugar solution, as it formed a very granular mass with water alone, which on drying out fell to pieces. These cylinders were burned in the electric furnace. No temperature measurements were made, but the specimens were examined with the microscope after each burn to observe the progress of the formation of tricalcium silicate. After one burn in the electric furnace, a nondusting mixture of beta-calcium orthosilicate and comparatively large round grains of free lime was found. After regrinding the powder was moistened with alcohol, remolded, and reburned for about five hours. This process was repeated three times before the material was found to be satisfactory. Entire homogeneity was never obtained, since the best product contained a few scattered grains of free lime, beta-calcium orthosilicate, and tricalcium aluminate. However, the hydration of these small amounts of impurities could in no way be confused with the hydration of the major portion of the product.

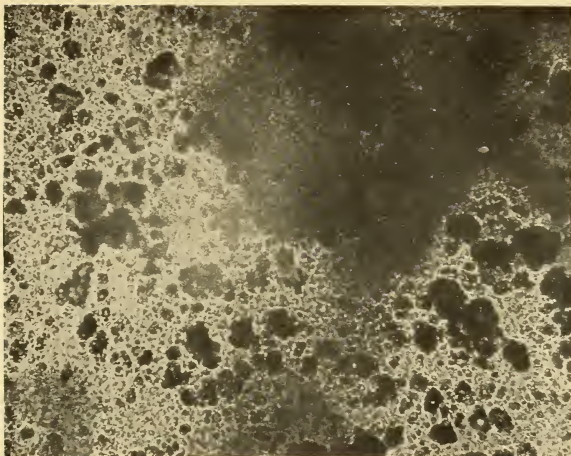


FIG. 15.—Showing amorphous, hydrated silicate on a slide of beta-calcium orthosilicate and tricalcium aluminate in water. The amorphous material covered the whole slide and obliterated the hydrated tricalcium aluminate crystals present. This was taken without nicols, and the magnification = 200 diameters

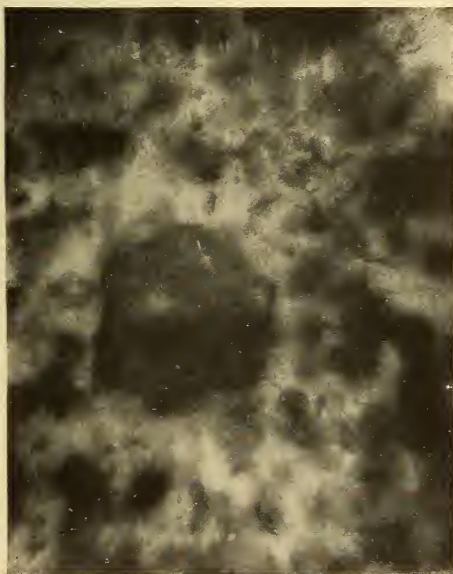


FIG. 16.—Showing tricalcium silicate and tricalcium aluminate in water, taken without nicols. Note the large hexagonal calcium hydroxide crystal and the smaller needles of hydrated tricalcium aluminate covered with and obscured by amorphous hydrated silicate. Magnification = 160 diameters



FIG. 17.—Showing tricalcium silicate and 5:3 calcium aluminate, taken with crossed nicols. Note the large calcium hydroxide crystals, the spherulites and needles of hydrated tricalcium aluminate. The amorphous material can not be observed with crossed nicols. Magnification = 165 diameters

The trisilicate consisted of minute crystallites, showing no definite crystal outline. The mean index of refraction was 1.715 ± 0.003 . The double refraction was extremely low, the maximum interference color observed being a first order grayish white, while many of the grains were practically isotropic. Interference figures were observed with difficulty on a few favorable grains, and the compound was found to be biaxial with a very small optic axial angle. The optical character is negative. No twinning lamellæ whatever were noted. The chemical analysis showed:

	Per cent.
SiO ₂	26.12
Al ₂ O ₃21
Fe ₂ O ₃09
CaO.....	72.62
MgO.....	.93
Ignition loss.....	.09

(B) *Hydration of Molded Specimens in Water.*—A noticeable feature of the hydration of the tricalcium silicate was the rapidity with which it took place. A specimen mixed with 20 per cent of water set hard at the end of five hours without any noticeable evolution of heat, and specimens kept 28 days in water showed no signs of cracking or disintegrating. This is in noticeable contrast to the mixtures of beta-orthosilicate with as much as 50 per cent high-burned free lime. In this case the material was soft and friable after 24 hours and fell away to a soft mush in the water; and very small amounts of amorphous hydrated silicate were found, while with the trisilicate large quantities were observed.

(C) *Hydration in Steam at Atmospheric Pressure and in the Autoclave with Water.*—On treating tricalcium silicate in steam at temperatures both below 140 and up to 200° C from 0.5 to 0.7 per cent of water was taken up. The fact that water was absorbed at high temperatures must be due to the hydration of the free lime present, as a small amount of calcium hydroxide was always found present after these tests.

In the autoclave, it was possible to hydrate completely the trisilicate after it was allowed to harden for 24 hours with water, so that no grains with unhydrated centers remained. The hydration products were crystals of calcium hydroxide and amorphous hydrated silicate. On the other hand, mixing the beta-orthosilicate

with one-third of high-burned lime showed the silicate to be almost completely unhydrated after the autoclave treatment. A further effect noted was that raising the pressure in the autoclave from 150 to 600 pounds per square inch resulted in an increased size of the calcium hydroxide crystals.

(D) *Hydration on Slide with Water.*—Hydrating the tricalcium silicate with water on a slide resulted in the formation of a few crystals of calcium hydroxide and amorphous hydrated silicate within 24 hours. The hydration continued with the formation of more and larger calcium hydroxide crystals and considerable amorphous material, until at the end of three weeks the latter covered the slide completely. The calcium hydroxide crystals were orientated generally in one of two ways, either perpendicular to the "c" crystallographic axis or parallel to it. When perpendicular to "c" they were hexagonal in shape, showed little or no double refraction, and gave typical uniaxial interference figures perpendicular to "c" with negative optical character. When parallel to the "c" axis they showed prismatic development, medium high interference colors often of the third order, depending upon the thickness of the crystals, parallel extinction and the interference figures consisted of two rapidly separating hyperbolæ characteristic of uniaxial crystals orientated parallel to "c." The amorphous material was gelatinous in appearance. No needles were observed.

(E) *Hydration with Plaster.*—Using the tricalcium silicate with plaster and varying the amount of the latter, no differences were noted except in the amount of gypsum crystals which increased with the percentage of plaster. This was the case with both slides and molded specimens. Hydration in the autoclave increased the size of the calcium-hydroxide crystals greatly.

(F) *Hydration with Limewater.*—Tricalcium silicate, hydrated on a slide with limewater, showed the same products as that hydrated in water. The rate of hydration was not apparently changed, since the amorphous material and calcium-hydroxide crystals began to be formed within 24 hours.

(G) *Influence of Tricalcium Silicate on Hydration of Beta-Calcium Orthosilicate.*—Mixing tricalcium silicate in varying amounts with beta-orthosilicate and plaster and hydrating in the autoclave had

no favorable influence on the hydration of the orthosilicate while the trisilicate was completely hydrated.

6. HYDRATION OF TRICALCIUM SILICATE AND ALUMINATES.

(A) *Hydration on Slides with Water.*—Slides containing mixtures of tricalcium silicate and tricalcium aluminate and of tricalcium silicate and 5:3 calcium aluminate were hydrated in the same manner as the individual constituents. The aluminates began to hydrate almost immediately to form the aforementioned hydration products. Within 24 hours the silicate began to take up water, splitting off calcium-hydroxide crystals and forming the amorphous hydrated silicate. (See Figs. 16 and 17.)

In order to dispel any doubt as to the identification of the hexagonal hydrated tricalcium aluminate and the hexagonal calcium hydroxide plate crystals, slides containing each of the above compounds were dried in an atmosphere free from carbon dioxide and then immersed in a liquid of refractive index equal to 1.555. The large hydroxide plates had invariably a higher and the small aluminate plates a lower index than the liquid. (See description of their optical properties, pp. 8, 23.)

(B) *Hydration of Molded Specimens in Water, Limewater, and Calcium Sulphate Solution.*—Monocalcium aluminate, 5:3 calcium aluminate, and tricalcium aluminate were mixed with the tricalcium silicate in the proportion of 1:3, gauged with 20 per cent water, pressed in the molds, left for 24 hours, and then immersed in distilled water for 28 days. They were then dried and examined microscopically. In each case calcium-hydroxide crystals were observed, and complete hydration of the tricalcium silicate had taken place. The specimens were extremely hard, dense, and strong, and compared very favorably to the strongest 28-day neat cement briquets. No differences were noted in cases where either limewater or calcium-sulphate solution were used for gauging. Only in the case of tricalcium aluminate and tricalcium silicate gauged in gypsum was there any considerable quantity of sulphoaluminate needles noted, but they were not well developed. In another case a saturated solution of tricalcium aluminate was used for gauging, the specimen being immersed in water. At the

end of 28 days it was very hard and compact, and the surface was coated with calcium hydroxide crystals large enough to be picked off.

With regard to their time of formation, calcium-hydroxide crystals could be observed in a specimen four hours after mixing with water, and they constantly grew in size. However, at the end of 28 days they were not as large as those produced in the autoclave at 300 pounds pressure after 24 hours' hardening.

In only one combination was disintegration observed, this taking place in a 3:1 mix of tricalcium silicate with tricalcium aluminate gauged with a saturated calcium-sulphate solution and immersed in saturated limewater. After 10 days the specimen was badly cracked, and after 15 days it had disintegrated to a soft mass containing large calcium hydroxide crystals, well developed hydrated tricalcium aluminate, and sulphoaluminate crystals with much isotropic amorphous material. Suspended in the solution was an abundance of very fine crystals of sulphoaluminate, so fine as to appear megascopically like a gelatinous precipitate.

(C) *Hydration on Slides with Limewater and Calcium Sulphate Solution.*—The hydration on slides of mixtures of tricalcium silicate with the aluminates in limewater and plaster solution gave no new hydration products except crystals of calcium sulphoaluminate. The rates of hydration did not differ from the rates of hydration of the same mixtures hydrated with water.

So far as could be noted, the calcium-hydroxide crystals have no effect on the precipitation of sulphoaluminate crystals. The former are more or less inert and are not readily acted upon by White's solution, while the amorphous calcium hydroxide reacts, forming the characteristic hydrated calcium phenolate crystals in a few minutes. (See Fig. 18.) However, calcium hydroxide crystals are slowly acted upon by magnesium salt solutions, and the amount of magnesium hydroxide precipitated is very small in comparison with that produced by the amorphous hydroxide.

Owing to the limited amount of material available, no tests were made to determine the amount of lime split off from the tricalcium silicate. Le Chatelier⁵² and others state the principal constituent of

⁵² Bull. Soc. Chim., 42, pp. 82-89; 1900.

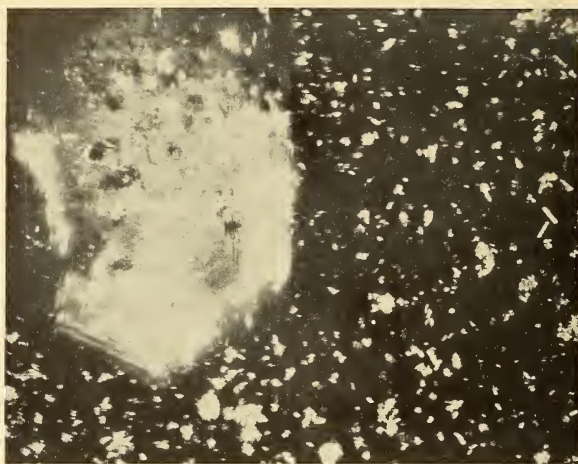


FIG. 18.—Showing White's test on crystallized and amorphous calcium hydroxide, taken with crossed nicols. The large hexagonal plate is crystallized calcium hydroxide and is not affected. The amorphous hydroxide has been entirely converted into the characteristic prismatic crystals of calcium phenolate. Magnification = 280 diameters

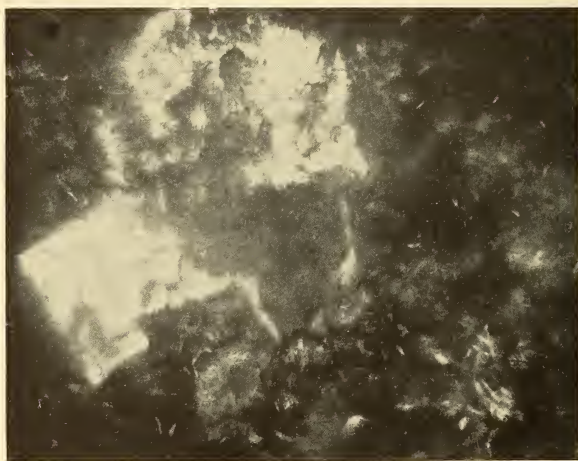


FIG. 19.—Showing a white cement hydrated in water, taken with crossed nicols. Note the large calcium hydroxide crystals and the smaller hydrated tricalcium aluminate needles. These are more or less obscured by amorphous material. Magnification = 280 diameters

hardened cements is a hydrated monosilicate ($\text{CaO} \cdot \text{SiO}_2 \cdot 2\frac{1}{2} \text{H}_2\text{O}$). On the other hand there is the work of Newberry and Smith,⁵³ who found that one sample of supposed trisilicate, after shaking with water, gave a varying residue of 1.5 to 2 equivalents of CaO. to 1 of SiO_2 and a fused sample gave a hydrated silicate of the composition of $2\text{CaO} \cdot \text{SiO}_2 \cdot 7\text{H}_2\text{O}$. In addition there is the interesting but little known work of Ferrari,⁵⁴ who found that the reaction proceeded as follows: $3\text{CaO} \cdot \text{SiO}_2 + \text{Aq} = 2\text{CaO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O} + \text{Ca}(\text{OH})_2$ and that the hydrated silicate formed yielded no more lime to water but lost lime on treatment with ammonium chloride solutions.

Again, Rebuffat⁵⁵ states that the calcium orthosilicate on hydrating does not decompose into calcium monosilicate and lime hydrate, since testing with sugar solutions showed that the composition of the material was very far from being calcium monosilicate.

IV. PORTLAND CEMENT

The hydration of cements were studied by slide tests, by the examination of molded specimens, and by means of the autoclave. For convenience in comparing the results they were tabulated, No. 1 being a white cement, No. 2 being another brand of white cement which contained 0.5 per cent CO_2 and 4 per cent H_2O , No. 3 a high silica slow-hardening cement, and No. 4 a dark-colored cement containing 8.97 per cent Fe_2O_3 and 3.64 per cent Al_2O_3 . The chemical analyses are as follows:

	No. 1	No. 2	No. 3	No. 4
	Per cent	Per cent	Per cent	Per cent
SiO_2	25.02	23.68	24.59	20.37
Al_2O_3	6.08	5.10	6.49	3.64
Fe_2O_3	0.49	0.37	2.64	8.97
CaO	62.89	62.69	61.04	61.41
MgO	1.11	1.96	1.71	0.82
SO_3	1.75	1.37	1.45	1.19
Na_2O	0.11	0.03	0.12	1.54
K_2O	0.56	0.30	0.40	0.24
CO_2	1.08	0.51	0.93	1.04
H_2O	0.95	4.08	0.75	1.06

⁵³ J. Soc. Chem. Ind., 22, p. 94; 1903.

⁵⁴ Ciment, 17, pp. 81-85; 1912.

⁵⁵ Tonind. Ztg. 26, p. 1579; 1902.

(A) *Hydration of Molded Specimens and Hydration in the Autoclave.*—The tabulated tests in Table 4 were made on fragments of briquettes made from neat cement and 18–20 per cent of water, stored in a damp closet for 24 hours, and then immersed in water. One of the interesting facts noted is the slow hydration of the beta-orthosilicate, the amount of which varies with different cements. Although a large number of samples have been examined, no definite rule has been evolved as to the rate of hydration of the beta-orthosilicate. Some cements contain a little hydrated beta-orthosilicate at the end of 7 days, while others contain very little at the end of 28 days. Some contain considerable unhydrated beta-orthosilicate at the end of 90 days. Perhaps the greatest factor resulting in the slowness of the beta-orthosilicate hydration in a cement is the size of grain. Microscopical evidence points to the fact that beta-orthosilicate in the larger cement grains is extremely slow to hydrate, while in the smaller grains it hydrates fairly readily. This is no doubt due to the comparatively small amount of surface that the large grains offer to the action of the aluminate solution. Again, the coating of amorphous hydrated calcium silicate appears to prevent the ready penetration of the water into the unhydrated interior of the grains.

The absorption of water by the different cements as tabulated below are of interest chiefly in connection with the autoclave hydration:

		No. 1	No. 2	No. 3	No. 4
		Per cent	Per cent	Per cent	Per cent
Hydration in water for..	24 hours.....	8.24	7.72	5.48	5.42
	7 days.....	10.88	8.84	8.92	9.74
	28 days.....	13.76	13.78	13.48	14.06
Hydration in autoclave.....		11.00	10.86	9.86	10.86

The amount of water absorbed by the autoclave briquettes is significant on account of the considerable amount absorbed, and by the fact that the refractive index of the aluminate was raised and the optical properties of the gypsum changed. This indicates conclusively that a part of the water has been expelled.

(B) *Hydration of Cement on Slides.*—Slides were made up of a commercial white cement in an excess of water. (See Fig. 19.) The first effect noted was the beginning of the formation of hydrated tricalcium aluminate and calcium sulphoaluminate crystals which took place in a short time. The latter crystals were extremely fine and could readily be overlooked. At 24 hours these crystals had increased in size and numbers and the presence of a few lime hydrate crystals, together with a little amorphous material, showed that the tricalcium silicate was beginning to hydrate, while the beta-orthosilicate was quite unchanged. With time the number of calcium hydroxide crystals and the amount of amorphous material increased. Finally the latter covered the whole slide.

A slide consisting of a normal Portland cement in water started to hydrate quickly with the formation of hydrated tricalcium aluminate and calcium sulphoaluminate crystals. The hydration of tricalcium silicate was slow in starting, since calcium hydroxide crystals and the accompanying amorphous hydrated silicate were noted only after two days. The further hydration of this compound proceeded readily with the formation of more calcium hydroxide and amorphous silicate. After a week the beta-orthosilicate in the fine cement grains began to hydrate to the amorphous silicate, and this latter covered practically the whole slide.

A sample of normal cement hydrated with an excess of water in a well-stopped bottle for over a year showed hydrated tricalcium aluminate needles and plates, sulphoaluminate needles, calcium hydroxide crystals, calcium carbonate crystals, and amorphous material. Thus, even in a considerable length of time, an excess of water did not bring about the crystallization of the amorphous hydrated silicate.

(C) *Use of Large Volumes of Mixing Water.*—The tricalcium silicate is in most cases only slightly hydrated at the end of 24 hours, while the beta-orthosilicate has not reacted at all. Therefore, the use of large volumes of mixing water, as is done in mixing concrete to be spouted or sent through chutes, can be considered only in relation to the aluminates. In these tests, it has

been found that variations in the amount of water affected only the rate at which the aluminates hydrated and crystalized, the larger the amount of water the more rapid the process, and as the aluminates crystalize eventually, it is better that the process take place before any considerable amount of rigidity has ensued in the cement, as there is less danger of strains being set up by the formation of crystals.

(D) *Regauging of Cement*.—Regauging is another process which likewise apparently affects only the aluminates. However, the results in the literature are varied, as in some cases it has been found to improve the strength of cements, and in other cases where continuous mixing has been employed the strength tests have fallen off. The effect of regauging is merely to hydrate a greater amount of aluminate than would be done by one mixing, but a very important fact is the amount of gypsum present. From this work it is very evident that the early strengths in cement are due not to the crystallization of the aluminates but to the formation of a dense, hard, amorphous mass of hydrated aluminate. Then it follows that the greater the amount of hydrated aluminate formed in 24 hours, the greater the early strength, and for this reason the high alumina cements always show high early strengths. It has already been noted that aluminates without gypsum set up almost instantaneously with water, but that a very small amount is hydrated. In other words, the grains hydrate along the edges and adhere, so that the addition of large amounts of water has little effect since it can but slowly permeate through the amorphous material which is formed. The addition of gypsum, however, allows a greater amount of water to penetrate toward the center of the grains before there is coagulation with the formation of the impermeable wall through which the water penetrates very slowly.

Manifestly, therefore, the slower setting the cement the less it will be benefited by remixing, as the effect of the latter is to mechanically remove the hydrated material from the surface of the grains, thus exposing a fresh surface to be hydrated. Conversely, a quick-setting cement will be benefited by remixing or continuous mixing, until a point is reached at which the cohesion be-

tween the hydrated particles is reduced. A cement takes up water very slowly, and if 20 per cent of water be used in mixing this is not combined even after the cement has hardened, but part of it is combined and part is mechanically held between the grains, where it slowly penetrates from the outside to the center of each grain. It is evident, therefore, that an excess of water is necessary for complete hydration. However, the greater the excess the less the cohesion between the particles of the hydrated material and the lower the resulting strength tests. Therefore, additions of gypsum to the cement and remixing the cement play the same rôle in allowing the access of water to the aluminate grains.

(E) *Retardation of Set Caused by Aeration.*—From the results obtained from steam tests on neat cements it has been found, as noted before, that only the aluminates and free lime were affected. The same results hold true for the aeration of cements. The slower set caused by aeration is due to the hydration of the free lime and to the absorption of a small amount of water by the aluminate grains, which thus form on their surface a thin layer of impermeable amorphous hydrated aluminate. When the cement is gauged with water, this thin layer retards the passage to the unhydrated center, a longer time ensues before hydration and coagulation takes place, and the initial set resulting from this coagulation is delayed.

(F) *The So-Called Abnormal Behavior in the Autoclave.*—It has been considered by several experimenters that the reactions taking place in the autoclave are abnormal and bear no relation to those taking place in normal hydration. In the considerable amount of work done with the autoclave there has been found no evidence of abnormal hydration, except in the partial dehydration of the gypsum and hydrated tricalcium aluminate. This has been overcome by filling the autoclave three-fourths full of water and immersing the briquettes, so that at all times during the test they are completely submerged in hot water. Under these conditions the crystals were very slightly altered. The aluminate crystals are very large, but no larger than those noted at the end of 28 days. On the other hand, the calcium hydroxide crystals are

much larger by the autoclave hydration than by normal hydration at 28 days. They do not lose water with the increase in temperature and pressure. By subjecting specimens to 600 pounds pressure for two hours large growths of calcium hydroxide crystals have been observed which could be removed with a pair of forceps. On the other hand, crystals of calcium hydroxide of equal size have been noted in briquettes which had been stored in sea water. The presence of salts in solution seems to favor the growth of large crystals of lime hydrate. Again, columnar aggregates growing out from the specimens have been observed in briquettes stored in fresh water for a considerable length of time. These consist of calcium carbonate evidently resulting from the carbonation of calcium hydroxide due to exposure. Wig⁵⁶ has stated that 150 pounds pressure produced the maximum strength in treated briquettes. Probably at this temperature and pressure the calcium hydroxide crystals would more nearly approximate those found by 28-day normal hardening. It has not been possible to confirm his strength tests, especially with high-silica cements, but it is found that there is an increased amount of hydrated silicate and higher strengths in briquettes at pressures much over 150 pounds. Probably his results would hold more nearly true with respect to higher alumina cements, in which the increase in temperature with increasing pressure would tend to dehydrate the aluminates.

With regard to the possible formation of a sand-lime brick bond in the specimens, as suggested by Cushman,⁵⁷ it is possible that such a reaction does take place, if there be sand present, but in the neat specimens this has never been noted. There is little, if any, uncombined silica in a normal cement which would be capable of combining with calcium hydroxide, and certainly not enough to affect the strengths in any way.

(G) *Action of Calcium Sulphoaluminate in Disintegration of Cement.*—Two other compounds play an important part in the hydration of cement, viz, the calcium sulphoaluminate and free lime. In considering the first compound, the disintegrating action which may accompany its crystallization has been greatly exaggerated.

⁵⁶ Eng. Record, 68, pp. 16-17; 1913.

⁵⁷ Eng. Record, 68, pp. 14-15; 1913.

The reason is that though the compound does crystallize with large amounts of water, the crystals produced in a hydrated cement are extremely small. Under the microscope the maximum length observed was never over 0.04 mm and the width never over 0.0025 mm, so that a suspension of the sulphoaluminate crystals has the appearance of a gelatinous precipitate. It is possible that in sea water or in alkaline water the presence of other salts in solution may assist in the development of larger crystals which might then exert an expansive force. Another fact which precludes their having any considerable disruptive action is that they begin to form simultaneously with the beginning of hydration of the aluminate, and before the cement mass has begun to assume any great rigidity.

In the disintegration of concrete by alkali, Jewett⁵⁸ has noted that failure is caused by the formation of crystals whose expansive force is enormous, but which disintegrates to a fine powder on exposure to air. The sulphoaluminate crystals probably play a part in this disintegration, although not through the expansive force of crystal growth. They form minute crystals, owing to their immediate precipitation from solution on coming in contact with limewater. These grow very little, so that any force produced must result from some other source, i. e., alkali sulphate or calcium hydroxide crystals. The sulphoaluminate crystals, however, lose water very readily and disintegrate to a fine powder. If they were present in large quantities in a cement, their drying out and disintegration would render the material very porous and readily allow the penetration of additional quantities of salt-bearing waters. Such a condition could only come about where the action of the alkali water was intermittent, allowing first a drying out and then a seepage of alkali. Framm⁵⁹ considers the presence of a small amount of sulphoaluminate crystals in cement as being beneficial, owing to the increased density which results from their presence.

(4) *Action of Free Lime in Accelerated Tests.*—The most interesting observations on the hydration of cements have been noted with regard to the behavior of free lime. This compound may

⁵⁸ Proc. Am. Soc. Testing Materials, 8, p. 480; 1909.

⁵⁹ Chem. Ztg., 35, p. 256; 1911.

or may not be present in a cement. It is generally noted in small amounts in well-burned higher limed cements and in underburned lower limed cements. On hydration free lime will, according to its fineness, hydrate as crystalline or amorphous calcium hydroxide. It is to this formation and particularly to the growth of large calcium hydroxide crystals that the disruption observed in accelerated tests must be attributed. Kuhl⁶⁰ has noted that expansion phenomena in cement are not due to the increase in volume owing to formation of amorphous calcium hydroxide, but result from pressure caused by growing crystals and *exerted in only one plane*. Ready confirmation of this in the autoclave tests has been found.

Where the free lime is distributed evenly throughout the cement the growth of crystals may be such as to cause a briquette to expand enormously in all directions, the expansion causing a decrease in cohesion of the cement particles until complete disintegration takes place, and the briquette falls to pieces as a coarse granular powder. In other cases, where there seems to be a segregation of free lime, the development of crystals may cause cracking.

This ability of lime to form either crystalline or amorphous calcium hydroxide on hydration, depending upon the physical characteristics of the lime, readily explains the behavior of various cements in the accelerated tests. For instance, (1) some cements will not pass the boiling test, (2) some will pass the boiling test but not the autoclave test, (3) and others will pass either test after seasoning where previously they would not. In the first case the free lime is sufficiently fine and high-burned so that in the boiling test it may hydrate, crystallize, and the growth of crystals may be sufficient to cause disintegration. In the second case, the free lime may be so coarse or highly burned as not to hydrate in the boiling test, but only in the autoclave due to the high pressure and temperature employed. In the third case, aeration with insufficient water to allow solution and crystallization may cause the free lime to hydrate to the amorphous condition. In the accelerated tests there is no formation of crystals from this amorphous material, hence no disintegration.

⁶⁰ Tonind. Ztg., 36, pp. 1331-1334; 1912.

Gano ⁶¹ has noted that defective pats stored in air and water after three months stood the boiling test perfectly. In these cases the hydration of the free lime was complete, so that there was no free lime to be affected by the boiling test. These defective pats might not have passed the boiling test at either 7 or 28 days, if the hydration of the free lime were not complete, owing to the fact that hot water accelerates the hydration of unhydrated lime sufficiently to cause a rapid growth of crystals and a corresponding disruption of the other hydrated material.

It has been stated that the aluminate crystals do not grow to nearly the same extent as do the calcium hydroxide crystals. It is very probable that the falling off in strengths noted between 7 and 28 days is due quite as much to the growth of calcium hydroxide crystals as it is to the growth of hydrated tricalcium aluminate crystals.

V. SUMMARY

The following summary and conclusions are made by the authors as a result of this investigation:

This investigation included the preparation of cement minerals in conditions as nearly pure and homogeneous as possible. They consisted of the following compounds: Free lime, tricalcium aluminate, 5:3 calcium aluminate, monocalcium aluminate, beta-calcium orthosilicate, gamma-calcium orthosilicate, and tricalcium silicate. The hydrations took place on microscopic slides with an excess of water, in a cylinder with steam at atmospheric pressure, and in the autoclave with steam at various temperatures and pressures. The compounds were also molded with quantities of water approximately those used in normal-consistency mixtures. Limewater and calcium sulphate solutions were also used as the hydration medium.

With an excess of water, tricalcium aluminate hydrates as the compound $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, where x varies with the drying conditions. 5:3 calcium aluminate and monocalcium aluminate, on hydrating, split off amorphous hydrated alumina and form the hydrated tricalcium aluminate. Under conditions such as typified by the molded specimens, the above crystallized compound does

⁶¹ Eng. News, 67, p. 930.

not form immediately, but separates from solution as an amorphous material. In steam at atmospheric pressure a little crystalline aluminate is formed with the amorphous material, still more in the autoclave, and finally, on microscope slides, the hydrated tricalcium aluminate is entirely crystallized. Wherever the amorphous aluminate is formed, it slowly but eventually changes to the crystallized compound.

The hydration of the aluminates begins readily in all cases. With an excess of water the reaction progresses rapidly, and in a few days the aluminates are completely hydrated. With restricted amounts of water, however, the individual aluminate grains become coated with amorphous hydrated aluminate, through which further action proceeds with more or less difficulty.

The tests in steam at atmospheric pressure showed that the weakly basic aluminates do not absorb water above 110°C , while the more basic aluminates absorb water up to 140°C . Furthermore, a specimen of tricalcium aluminate containing high-burned free lime absorbs water even at 175°C .

The nature of the calcium hydroxide, formed by the hydration of free lime with much water, depends upon the fineness of the lime grains and the burning temperature. With coarser lime grains and with highly burned lime the hydration produces a preponderance of crystallized calcium hydroxide. On the other hand, with fine lime grains and with low-burned lime, mainly amorphous hydroxide is formed. Calcium hydroxide crystals are much more inactive chemically than the amorphous variety. White's solution, which attacks the amorphous hydroxide almost instantly, reacts extremely slowly with the crystals. In the autoclave the amorphous variety is not changed, whereas free lime yields according to its fineness and burning temperature crystallized and amorphous hydroxide. The crystals here often grow to large size, depending upon the length of time of reaction, the temperature, and the pressure.

The hydration of the aluminates in limewater reveals the same compounds as in distilled water. No new type of crystals which might indicate hydrated tetracalcium aluminate was observed. There does seem to be an action, however, between the hydrated

alumina split off and the calcium hydroxide of the solution, resulting in a greater development of crystallized hydrated tricalcium aluminate.

Aluminates hydrated in the autoclave with an excess of lime-water give no new type of compound. The plate crystals of hydrated tricalcium aluminate are rather poorly developed. The addition of dry calcium hydroxide up to 50 per cent decidedly retards the crystal growth of the aluminates in the autoclave.

The first effect of gypsum solution on the aluminates is to retard the formation of amorphous hydrated material and keep the pores of the material open to the further penetration of water. Specimens hydrated in saturated gypsum solutions show the highest ignition loss after six days. The products of hydration are the same as those with distilled water, with the exception of the additional formation of sulphoaluminate needles. This new compound is identical for all three aluminates, and its formula is $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot x\text{H}_2\text{O}$. The formation of this compound is only incidental to the initial set and not the cause of its retardation, since the compound is formed before, during, and after the set. Variation of the gypsum content above and below a certain definite concentration causes a decrease in the setting time.

The problem of initial set is probably one involving the action of small amounts of electrolytes in retarding the coagulation of the amorphous aluminate material. The evidence is in favor of the fact that the aluminates coagulate and separate as amorphous bodies from supersaturated solutions, the rate of coagulation being affected by such small quantities of electrolyte as to preclude the possibility of the reaction being solely a chemical one. Thus with a certain and definite concentration of gypsum, maximum hydration is attained, and at the same time the rate of coagulation is retarded, increasing the time of set.

The sulphoaluminate crystals are broken up in the autoclave, as is also gypsum. Club-shaped crystals are noted with optical constants that suggest a composition between gypsum and anhydrite. With higher temperatures and pressures water is even driven out of the amorphous hydrated aluminate. Gypsum favors the growth of hydrated tricalcium aluminate crystals in the autoclave.

Calcium metasilicate, as well as gamma-calcium orthosilicate, is practically inert with regard to hydration. Beta-calcium orthosilicate is but slightly hydrated in water after a considerable length of time. This is manifested by a slight etching of the grains and the formation of a small amount of amorphous material. The action of limewater and plaster solution does not materially increase the hydration. The treatment of this silicate with tricalcium aluminate solution gives maximum hydration and the best 28-day test pieces. In mixtures of the beta-orthosilicate and the aluminates the latter show some hydration while the former is unhydrated after 24 hours, at which time cements are exposed to accelerated tests. At 28 days the aluminates are completely hydrated, and the silicate shows quite a little hydration. The test pieces, while exhibiting fairly good rigidity, have not the strength of corresponding cement briquettes. The slides of beta-calcium orthosilicate and aluminates indicate that the hydration of the aluminates proceeds as previously noted. With an excess of water the silicate hydrates more quickly than with limited water, the product being the same amorphous gel-like material.

Homogeneous tricalcium silicate was not obtained, the most satisfactory product containing an extremely small amount of free lime, beta-orthosilicate and tricalcium aluminate. Tricalcium silicate acts entirely differently from either beta-orthosilicate or mixtures of beta-orthosilicate and lime, with respect to hydration. It hydrates readily with excess of water, with limited water, and in the autoclave. The products of hydration are identical and consist of calcium hydroxide crystals and amorphous hydrated silicate. No hydrated calcium metasilicate needles are observed. It sets hard in 5 hours and shows no sign of disintegration after 28 days in water, in the autoclave. The size of the calcium hydroxide crystals depends upon the pressure. In general the greater the pressure the larger the crystals. Mixing tricalcium silicate with beta-calcium orthosilicate has no favorable effect on the hydration of the latter.

Mixtures of tricalcium silicate and the aluminates gauged with water, lime water, and plaster solution show first the beginning of hydration of the aluminate, followed shortly by the hydration of

the silicate. The 28 specimens are extremely dense, hard, and strong, comparing very favorably with the strongest neat cement briquets.

The hydration of cements is thus brought about by the formation of amorphous hydrated tricalcium aluminate with or without amorphous alumina, the aluminate later crystallizing. At the same time sulphoaluminate crystals are formed, and low-burned or finely ground lime is hydrated. The formation of the above compounds begins within a short time after the cement is gauged. The next compound to react is tricalcium silicate. Its hydration may begin within 24 hours, and it is generally completed within 7 days. Between 7 and 28 days the amorphous aluminate commences to crystallize and beta-orthosilicate begins to hydrate. Although the latter is the chief constituent of the American Portland cements, it is the least reactive compound. The early strength (24 hours) of cements is probably due to the hydration of free lime and the aluminates. The increase in strength between 24 hours and 7 days depends upon the hydration of tricalcium silicate, although the further hydration of aluminates may contribute somewhat. The increase between 7 and 28 days is due to the hydration of beta-calcium orthosilicate, but here are encountered opposing forces, in the hydration of any high-burned free lime present and in the crystallization of the aluminate. It is to this hydration that the falling off in strength between 7 and 28 days of very high-burned high limed cements is due, whereas the decrease shown by the high alumina cements is due to the crystallization of the aluminate. Finally, the iron in the cement is resistive to hydration and does not form any definite crystalline hydration products, but occurs as a rust-like material.

The last statement is perfectly true for the *cements we have examined* and contains nothing derogatory to the so-called iron cements.

WASHINGTON, April 18, 1914.

TABLE 1
Showing Hydration of Aluminates

	Slides	Steam at atmospheric pressure	Autoclave.	Molded specimens
Tricalcium aluminate.	With water....	Needles and hexagonal plates of hydrated tricalcium aluminate. No amorphous material.	Considerable amorphous material, a few needles, and plates. No unhydrated material.	Hydration product after 24 hours entirely amorphous, grains showing unhydrated centers and hydrated edges.
	With lime-water.	Same constituents as with water. No new type of crystals denoting hydrated tetra-calcium aluminate.	No tests made.....	7-day specimens still contain a few unhydrated grains. Hydrated material is mainly amorphous with a few small plates and needles; 28-day specimens are completely hydrated and show increase in needles and plates.
	With plaster solution.	Crystals of hydrated tricalcium aluminate formed together with extremely fine needles of calcium sulphoaluminate.do.....	7-day specimens show very little unhydrated aluminate. Hydration products are both crystalline and amorphous hydrated tricalcium aluminate and calcium sulphoaluminate crystals.
	With water....	Needles, plates, and radial spherulites of hydrated tricalcium aluminate and some amorphous material (hydrated alumina).	Absorbs water to 140°. Splits off hydrated alumina and forms hydrated tricalcium aluminate. Considerable unhydrated aluminate.	After 24 hours chiefly amorphous material, very little crystal development. Unhydrated centers.
	With lime-water.do.....	With lime-water product same as above. With solid calcium hydrate crystallization is retarded and amorphous material increased.	7-day specimens contain a little unhydrated aluminate, also amorphous material and a few hydrated tricalcium aluminate crystals; 28-day specimens
5:3 calcium aluminate.				

With plaster solution.	Hydration products are crystals of hydrated tricalcium aluminate, amorphous hydrated alumina and sulphoaluminate crystals.do.....	Sulphoaluminate crystals destroyed. Quite a quantity of hydrated tricalcium aluminate crystals noted. Amorphous material and club-shaped crystals of $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$.	mens are completely hydrated and show considerable increase in needles and plates. 7-day specimens show a little unhydrated material. Hydration products are crystallized hydrated tricalcium aluminate and amorphous hydrated material, also sulphoaluminate.
With water...	Crystallized material consists of needles, plates, and spherulites of hydrated tricalcium aluminate. Also considerable amorphous hydrated alumina.	Absorbs water to 110° with formation of amorphous hydrated alumina crystalline hydrated tricalcium aluminate. Considerable unhydrated material noted. No tests made.....	Considerable amorphous material, also needles and plates of hydrated tricalcium aluminate.	Hydration product after 24 hours almost entirely amorphous, with few needle crystals.
With lime-water.do.....do.....	With lime-water same products as with water. Solid calcium hydrate up to 50 per cent favors the formation of amorphous hydrated material.	7-day specimens contain a little unhydrated material, much amorphous material, and quite considerable crystallized hydrated tricalcium aluminate in greater amount than in corresponding water specimen; 28-day specimens contain no unhydrated material.
With plaster solution.	Crystals of hydrated tricalcium aluminate. Considerable amorphous hydrated alumina and well-developed crystals of calcium sulphoaluminate.do.....	Contains a few hydrated tricalcium aluminate crystals, considerable amorphous material, and club-shaped crystals.	7-day specimens are all hydrated and consist of amorphous material, needles, and plates of hydrated tricalcium aluminate, also calcium sulphoaluminate crystals.

Monocalcium aluminate.

TABLE 2
Showing Hydration of Silicates

	Slides	Steam at atmospheric pressure	Autoclave	Molded specimens
Calcium meta-silicate.	With water....	No hydration.....	Extremely slight etching.....	No hydration.
	With lime-water.	No tests.....	No tests.....	No tests.
	With plaster solution.	do.....	do.....	Do.
	With water....	Extremely slight hydration (0.52 per cent water absorbed).	Trace of hydration.....	No hydration.
Gamma-calcium ortho-silicate.	With lime-water.	No tests.....	No tests.....	No tests.
	With plaster solution.	do.....	do.....	Do.
	With water....	No hydration.....	Slight etching and formation of minute quantity of amorphous material.	No hydration.
	With lime-water.	do.....	do.....	28-day specimens consist almost entirely of unhydrated beta-orthosilicate with a little amorphous material.
Beta-calcium orthosilicate.	With plaster solution.	do.....	do.....	Do.
	With tricalcium aluminate solution.	No tests.....	No tests.....	28-day specimens show much greater hydration of orthosilicate with formation of amorphous hydrated material, but no calcium hydroxide. Beta-orthosilicate shaken with large excess of solution for 10 days shows maximum hydration and ignition loss of 4.04 per cent.

Tricalcium silicate.	With water....	Started to hydrate within 24 hours with formation of crystals of calcium hydroxide and amorphous hydrated silicate. After three weeks hydration the slide was covered with amorphous material.	A slight amount of water absorbed at 140 and up to 200°, due to hydration of free lime present.	Hydration products are amorphous hydrated calcium silicate and crystals of calcium hydroxide whose size increase with increase in pressure. Completely hydrated.	Specimens with 20 per cent water set hard at the end of five hours showed no disintegration after 28 days. Hydration products are amorphous hydrated calcium silicate and crystallized calcium hydroxide.
With lime-water. With plaster solution.	do.....do.....	No tests made.....do.....	No tests made..... Products are the same as with tricalcium silicate hydrated in the autoclave with water except for the additional formation of $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$.	No tests made. Specimens with 20 per cent plaster solution set up hard and showed no disintegration at end of 28 days. Hydration products same as with hydration in water.
Tricalcium silicate and beta-calcium orthosilicate with plaster.				Trisilicate completely hydrated. Orthosilicate very slightly hydrated.	

TABLE 3
Showing Hydration of Silicates and Aluminates

	Slides	Steam at atmospheric pressure	Autoclave	Molded specimens
Calcium meta-silicate and aluminates.	With water....	No tests made.....	No tests made.....	No tests made.
	With lime-water.	do.....	do.....	Do.
	With plaster solution.	do.....	do.....	Do.
	With water....	do.....	do.....	Do.
Gamma-calcium ortho-silicate and aluminates.	With lime-water.	do.....	do.....	Do.
	With plaster solution.	do.....	do.....	Do.
	With water....	do.....	do.....	Do.
	With water....	do.....	do.....	Do.
Beta-calcium orthosilicate and aluminates.	Aluminates began to hydrate first to usual hydration products. Silicate began to be etched in less than a week, and amorphous hydrated silicate was formed. At end of three weeks silicate covered the whole slide.	Aluminates hydrated to quite an extent. Silicate unhydrated.	Aluminates hydrated. Orthosilicate but slightly etched.	28-day specimens somewhat friable. Aluminates hydrated entirely to usual hydration products. Silicate hydrated to quite an extent.

With lime-water.do.....	No tests made.....	No tests made.....	Same as with water, with a slight increase in amount of hydrated material.
With plaster solution.	Same as with water, with the additional formation of calcium sulphoaluminate crystals.do.....	Same as with water, but for the additional formation of $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$ crystals.	Same as with water, with the formation of sulphoaluminate needles.
With water....	Aluminates began to hydrate first. Trisilicate started to hydrate within 24 hours to calcium hydroxide and amorphous hydrated silicate. The latter covered slide in a week.	Aluminates hydrated to quite an extent. Trisilicate slightly hydrated.	Both silicate and aluminate hydrated. Calcium hydroxide crystals grow to large size.	28-day specimens hard and compact. Show complete hydration of silicate and aluminate. Amorphous aluminate has begun to crystallize. Amorphous hydrated silicate noted, also calcium hydroxide crystals.
With lime-water.do.....	No tests made.....	No tests made.....	Same as with water.
With plaster solution.	Same as with water, with the additional formation of sulphoaluminate crystals.do.....	Same as with water, but with the additional formation of $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$ crystals.	Same as with water, with the additional formation of sulphoaluminate crystals.

Tricalcium silicate and aluminates.

TABLE 4
Showing Hydration of Cements

	No. 1	No. 2	No. 3	No. 4
24 hours..	<p>No calcium hydroxide crystals, a little isotropic amorphous hydrate. Trisilicate hydrate very slightly hydrated. Orthosilicate unhydrated. Aluminate considerably hydrated to amorphous material. No needles or plates present.</p> <p>(A large number of calcium hydroxide crystals and some amorphous hydrate. Trisilicate all hydrated. Orthosilicate slightly hydrated. Aluminate all hydrated to amorphous material with a few needles and plates.</p>	<p>Some amorphous calcium hydroxide. No crystals. Amorphous hydrated trisilicate in a t e ; trisilicate slightly hydrated. Orthosilicate unchanged.</p> <p>Calcium hydroxide crystals not as well developed as in No. 1 (seven days); amorphous hydroxide. Trisilicate almost all hydrated. Aluminate hydrated to a few needles and plates and much amorphous material.</p>	<p>Very little amorphous calcium hydroxide. Aluminate hydrated to amorphous material. Trisilicate and orthosilicate unhydrated.</p> <p>Calcium hydroxide crystallized and small amounts of amorphous hydroxide noted. Trisilicate all hydrated. Orthosilicate very slightly hydrated. Aluminate hydrated to amorphous material with a few needles and plates.</p>	<p>A few small calcium hydroxide crystals with some amorphous hydrate. Trisilicate hydrated a little. Orthosilicate unhydrated. Trialuminate nearly all hydrated to amorphous material.</p> <p>Calcium hydroxide crystals large and more plentiful than in No. 4 (24-hours sample). Amorphous hydroxide. Trisilicate all hydrated. Orthosilicate slightly hydrated. Hydrated aluminate consisted of amorphous material with some needles and plates.</p>
7 days....	<p>Large amount of calcium hydroxide crystals and some amorphous hydroxide. Trisilicate all hydrated. Orthosilicate considerably hydrated, the hydrated silicate product in both cases being amorphous. Aluminate nearly all in fine needles and plates, a smaller amount being still amorphous.</p>	<p>Large crystals of calcium hydroxide. Some amorphous calcium hydroxide. Trisilicate all hydrated. Orthosilicate not very greatly hydrated. Hydrated aluminate needles and small plates rather plentiful.</p>	<p>Plenty of calcium hydroxide crystals and a little amorphous hydroxide. Trisilicate all hydrated. Orthosilicate partly hydrated and surrounded by amorphous material. Trialuminate present as needles, plates, and amorphous material.</p>	<p>A large number of calcium hydroxide crystals and some amorphous hydroxide. Trisilicate all hydrated. Quite a little orthosilicate still unhydrated. Aluminate as needles, plates, and amorphous material. Iron material slightly hydrated to opaque material being reddish and resembling iron rust.</p>
28 days....				

Autoclave after 24 hours in damp closet.	Very large calcium hydroxide crystals and some amorphous hydroxide. Orthosilicate all hydrated. Orthosilicate considerably hydrated. Aluminate all hydrated to amorphous material and needles.	Large calcium hydroxide crystals, some amorphous hydroxide. Trisilicate but slightly hydrated. Trialuminate all hydrated to amorphous material and needles.	Calcium hydroxide crystals larger than any of the others. Some amorphous hydroxide. Trisilicate hydrated. Orthosilicate partially hydrated. Trialuminate hydrated to amorphous material and needles.	Large calcium hydroxide crystals, some amorphous hydroxide. Trisilicate all hydrated. Much orthosilicate still unhydrated. Hydrated trialuminate needles and amorphous material observed. Iron material hydrated to reddish opaque fine-grained product.
--	---	---	--	--

NOTE.—Sulphoaluminate crystals observed in all specimens except those in the autoclave, where they are destroyed and $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$ formed.

(Continued from p. 2 of cover.)

33. The Determination of Carbon in Steels and Iron by the Barium Carbonate Titration Method (12 pp.).....J. R. Cain
34. Determination of Ammonia in Illuminating Gas (23 pp.).....J. D. Edwards
35. Combustion Method for the Direct Determination of Rubber (11 pp.)...L. G. Wesson
36. Industrial Gas Calorimetry (150 pp.).....C. W. Waidner and E. F. Mueller
37. Iodine Number of Linseed and Petroleum Oils (17 pp.).....
W. H. Smith and J. B. Tuttle
38. Observations on Finishing Temperatures and Properties of Rails (63 pp.)...
G. K. Burgess, J. J. Crowe, H. S. Rawdon, and R. G. Wallenberg
39. Analysis of Printing Inks (20 pp.).....J. B. Tuttle and W. H. Smith
40. The Veritas Firing Rings (10 pp.).....A. V. Bleininger and G. H. Brown
41. Lead Acetate Test for Hydrogen Sulphide in Gas...R. S. McBride and J. D. Edwards
42. Standardization of No. 200 Cement Sieves.....R. J. Wig and J. C. Pearson
43. Hydration of Portland Cement.....A. A. Klein and A. J. Phillips

CIRCULARS ISSUED BY THE BUREAU OF STANDARDS, DEPARTMENT OF COMMERCE

1. Verification of Standards and Measuring Instruments.
2. Measurements of Length and Area, Including Thermal Expansion.
3. Verification of Standards of Mass.
4. Verification of Standards of Capacity.
5. Testing of Clinical Thermometers.
6. Fees for Electric, Magnetic, and Photometric Testing.
7. Pyrometer Testing and Heat Measurements.
8. Testing of Thermometers.
9. Testing of Glass Volumetric Apparatus.
10. Legal Weights (in pounds) per Bushel of Various Commodities.
11. The Standardization of Bomb Calorimeters.
12. Verification of Polariscopic Apparatus.
13. Standard Specifications for the Purchase of Incandescent Lamps.
14. Samples of Analyzed Irons and Steels—Methods of Analysis.
15. A Proposed International Unit of Light.
16. The Testing of Hydrometers.
17. Magnetic Testing.
18. Standard Gauge for Sheet and Plate Iron and Steel.
19. Standard Density and Volumetric Tables.
20. Testing of Electrical Measuring Instruments.
21. Precision Measurements of Resistance and Electromotive Force.
22. Standard Specifications for Transformers, Oil-immersed, Self-cooled, 60-cycle,
2,200 Volts.
23. Standardization of Electrical Practice in Mines.
24. Publications of the Bureau of Standards.
25. Standard Analyzed Samples—General Information.
26. Analyzed Iron and Manganese Ores—Methods of Analysis.
27. The Testing and Properties of Optical Instruments.
28. The Determination of the Optical Properties of Materials.
29. Announcement of a Change in the Value of the International Volt.
30. Lime: Its Properties and Uses.
31. Copper Wire Tables.
32. Standard Regulations for Manufactured Gas and Gas Service.
33. United States Government Specifications for Portland Cement.
34. The Relation of the Horsepower to the Kilowatt.
35. Melting Points of Chemical Elements.
36. The Testing and Properties of Electrical Condensers.
37. Electric Wire and Cable Terminology.
38. The Testing of Mechanical Rubber Goods.
39. Specifications for and Measurement of Standard Sieves.
40. Sodium Oxalate as a Standard in Volumetric Analysis.
41. Testing and Properties of Textile Materials.
42. Metallographic Testing.
43. The Metric Carat.
44. Polarimetry.
45. The Testing of Materials.
46. Testing of Barometers.
47. Units of Weight and Measure; Definitions and Tables of Equivalents.
48. Standard Methods of Gas Testing.
49. Safety Rules to be Observed in the Operation and Maintenance of Electrical
Equipment and Lines.
50. National Standard Hose Couplings and Fittings for Public Fire Service.
51. Measurement of Time and Tests of Timepieces.